

*United States Court of Appeals
for the Second Circuit*



**PLAINTIFF'S
EXHIBITS**

74-1050

United States Court of Appeals

For the Second Circuit.

THE GENERAL TIRE & RUBBER COMPANY,
Plaintiff-Appellant,
v.

JEFFERSON CHEMICAL COMPANY, Inc.,
Defendant-Appellee.

ON APPEAL FROM THE UNITED STATES DISTRICT COURT FOR
THE SOUTHERN DISTRICT OF NEW YORK.

PLAINTIFF'S EXHIBITS.

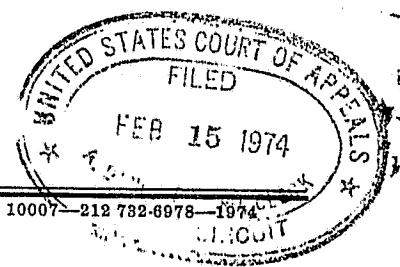
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PLAINTIFF'S EXHIBIT 1

U. S. Patent No. 3,102,875, Herbert L. Heiss

Pages 501a to 506a

United States Patent Office

3,102,875

Patented Sept. 3, 1963

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3,102,875

POLYURETHANE REACTION PRODUCT AND METHOD FOR MAKING SAME

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No Drawing. Filed Aug. 7, 1953, Ser. No. 373,836
12 Claims. (Cl. 260—77.5)

The present invention relates to a new series of resins, compositions of matter containing same and to the method of preparing such products.

The products of this invention are suitable for casting or pouring into intricate forms or crevices and are adapted for use in numerous applications, for example, as adhesives, protective coatings, components of insulating varnishes, impregnants for fibrous material to impart water resistance, flame resistance and improved hand thereto; as insulating and dielectric elements in transformers, capacitors, electrical terminals or bushings, cables or other electric devices; and as foamed-in-place resins. The products of relatively low molecular weight, that is, those derived from monoamines, monohydroxy compounds or monomercaptans, find use as plasticizers for vinyl resins and numerous other plastic materials.

In accordance with the instant invention, the new products are prepared by reacting an organic compound containing at least one urethane or thiourethane group with a compound of the general formula: R_n(NCX)_m, wherein R is an organic radical free from functional groups other than —NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, the second-mentioned reactant being employed in an amount sufficient to react with the urethane and/or thiourethane groups of the first-mentioned reactant. More specifically, the new products are prepared by reacting an organic compound containing a plurality of urethane and/or thiourethane groups with a compound of the above general formula wherein n is an integer having a value of at least 2, the second-mentioned reactant being employed in an amount sufficient to react with at least two urethane groups or one thiourethane group of the first-mentioned reactant.

The organic compounds containing at least one urethane or thiourethane group and preferably a plurality of these groups may be prepared in any suitable manner. For example, compounds containing urethane groups are prepared by reacting an organic hydroxy compound, preferably an organic polyhydroxy compound, with polyisocyanates, carbamyl halides such as carbamyl chloride, urea or substituted ureas; or by reacting mono- or polyamines with halocarbonates such as chlorocarbonates. Compounds containing thiourethane groups are prepared by reacting polyisocyanates with mercaptans or polymercapto compounds.

As illustrative examples of suitable hydroxy compounds for use in the production of organic compounds containing urethane groups, there may be mentioned methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, amyl alcohol, hexyl alcohol, octyl alcohol, decyl alcohol, lauryl alcohol, allyl alcohol, oleyl alcohol, tri-decyl alcohol, stearyl alcohol, methyl ricinoleate, ethyl lactate, diglycerides, monoesters of glycols, phenols, substituted phenols, alkylene oxide condensates of these hydroxy compounds, ethylene glycol, propylene glycol, butylene glycol-2,3, butylene glycol-1,3, 2-methyl pentanediol-2,4, 2-ethylhexane-diol-1,3, hexamethylene glycol, styrene glycol, N-phenyldiethanolamine, catechol, resorcinol, 2, 2-bis(4-hydroxyphenyl)propane, p,p'-dihydroxybiphenyl, decamethylene glycol; polyglycols (ether glycols) such

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as polyethylene glycols, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethyleneglycols 200, 400 and 600; polypropylene glycols, dipropylene glycol, tri-propylene glycol, polypropylene glycols 400, 750, 1200 and 2000; carbowaxes 1000, 1000W, 1500; monoethers of trihydroxy compounds such as glyceryl- α -allyl ether, glyceryl- α -phenyl ether, glyceryl- α -isopropyl ether; hydroxy esters such as an ester prepared from 1 mol of dibasic acid and 2 mols of a glycol or polyglycol, a polyester prepared so that the molar ratio of glycol or polyglycol to the dibasic acid is between 2 and 1, an ester prepared from 1 mol of a dimer acid and 2 mols of a glycol or polyglycol, an ester prepared from a hydroxy acid and a glycol or polyglycol so that the molar ratio of the glycol or polyglycol to the hydroxy acid is between 0.5 and 1 and an ester prepared from 1 mol of a trihydroxy compound and 1 mol of a monobasic acid, such as the monoglycéride of eleostearic acid; trihydroxy compounds such as glycerine, triethanolamine, pyrogallol, phloroglucinol, etc., alkylene oxide condensates of glycerine, triethanolamine, pyrogallol, phloroglucinol, etc.; monoethers of tetrahydroxy compounds; esters prepared from hydroxy acid and a trihydroxy compound so that the molar ratio of the latter to the former is between 0.33 and 1, such as glycerine triricinolate, esters prepared from 1 mol of a monobasic acid and 1 mol of a tetrahydroxy compound; tetrahydroxy compounds such as pentaerythritol, etc., alkylene oxide condensates of pentaerythritol, etc., esters prepared from 1 mol of a dibasic acid and 2 mols of a trihydroxy compound; pentahydroxy compounds, such as arabitol, xylitol, etc.; hexahydroxy compounds such as sorbitol, dulcitol and mannitol, etc.

Examples of suitable compounds which may be reacted with polyisocyanates to form thiurethanes are methyl mercaptan, ethyl mercaptan, butyl mercaptan, octyl mercaptan, cyclohexyl mercaptan, octadecyl mercaptan, allyl mercaptan, phenyl mercaptan, tolyl mercaptan, α -naphthyl mercaptan, dimercaptoethane, 1,2,3-trimercaptopropane, 1,2,3-trimercaptobutane, 1,5-dimercapto-3-(mercaptoethyl)pentane, 1,6-dimercaptohexane, 1,10-dimercaptodecane, 1,6-dimercapto-3-methylhexane, 1,4-dimercaptobenzene, dimercaptoxylylene, and polyvinyl mercaptan.

Illustrative examples of suitable isocyanates, isothiocyanates, carbamyl chlorides, and ureas which may be employed in the production of organic compounds containing urethane or thiourethane groups are ethyl, methyl, propyl, butyl, amyl, octyl, decyl, dodecyl, hexadecyl, octadecyl, allyl, isobutyl, isoamyl, cyclohexyl, phenyl, p-tolyl, p-chlorophenyl, m-chlorophenyl and α -naphthyl isocyanates, etc.; ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, etc.; and the corresponding diisothiocyanates; alkylene diisocyanates and diisothiocyanates, such as propylene-1,2-diisocyanate, butylene-1,2-diisocyanate, butylene-1,3-diisocyanate, butylene-2,3-diisocyanate, and butylene-1,3-diisothiocyanate; alkylidene diisocyanates and diisothiocyanates, such as ethylidene diisocyanate, butylidene diisocyanate and ethylidene diisothiocyanate; cycloalkylene diisocyanates and diisothiocyanates, such as cyclopentylene-1,3-diisocyanate, cyclohexylene-1,2-diisocyanate, cyclohexylene-1,3-diisocyanate, cyclohexylene-1,4-diisocyanate, and cyclohexylene-1,2-diisothiocyanate; cycloalkylidene diisocyanates and diisothiocyanates, such as cyclopentylidene diisocyanate, cyclohexylidene diisocyanate and cyclohexylidene diisothiocyanate; aromatic diisocyanates and diisothiocyanates, such as m-phenylene diisocyanate, p-phenylene diisocyanate, 1-methyl-2,4-phenylene diisocyanate, naphthylene-1,4-diisocyanate, di-phenylene-4,4'-diisocyanate or p-phenylene diisothiocyanate; aliphatic-aromatic diisocyanates or diisothiocyanates, such as xylylene-1,4-diisocyanate, xylylene-1,3-di-

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isocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-di-phenylpropane diisocyanate or xylylene-1,4-diisothiocyanate; methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, phenyl, cyclohexyl, p-chlorophenyl carbamyl chlorides; m-phenylene, p-phenylene, 2,4-toluylene, 4'4'-xylylene bis-carbamyl chlorides; urea, methylurea, ethylurea, butylurea, phenylurea, α -naphthylurea, cyclobenzylurea, α -dimethylurea, α -dicyclohexylurea, α -diphenylurea, 1,3-methylethylurea and 1,3-ethylphenylurea, etc.

Examples of amines which may be used in the preparation of organic compounds containing urethane groups are: methyl, ethyl, butyl, octyl, cyclohexyl, octadecyl, allyl amines, aniline, p-toluidine, substituted anilines and α -naphthylamine; ethylene diamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine, octamethylene diamine, decamethylene diamine, dodecamethylene diamine, N,N'-dimethyl decamethylene diamine, N,N'-dibenzyl hexamethylene diamine, cyclohexylene-1,4-diamine, ortho-phenylene diamine, m-phenylene diamine, p-phenylene diamine, benzidine, naphthalene-1,4-diamine, γ,γ -diamino dibutyl oxide, γ,γ -diamino dibutyl sulfide, diethylene triamine and triethylene tetramine, etc.

As typical examples of halocarbonates which may be reacted with amines to form organic compounds containing urethane groups, there may be mentioned methyl, ethyl, propyl, isopropyl, butyl, cyclohexyl, phenyl, p-tolyl and p-chlorophenyl chlorocarbonates and butylene-1,4-and hexylene-1,6-bis-chlorocarbonates, etc.

The organic compounds containing urethane and/or thiourethane groups used in the practice of the instant invention are preferably prepared by reacting an organic compound of the general formula: R(NCX)_n with an organic polyhydroxy and/or polymercapto compound in the proportions providing a ratio of —NCX groups to active hydrogen atoms which is greater than 1:1 but is desirably within the range of 1.1:1 to n :1. More specifically, these reactants are employed in the proportions providing a ratio of —NCX groups to active hydrogen atoms which falls in the range of about 1.3:1 or 1.5:1 to about n :1 and preferably within the range of about 2:1 to about n :1. The products obtained by this reaction are adducts which contain urethane and/or thiourethane groups and also free isocyanate and/or isothiocyanate groups. Therefore, these products can be converted into more highly polymerized products by bringing out a reaction between the isocyanate and/or isothiocyanate groups of one molecule with the urethane and/or thiourethane groups of the same or another molecule. This is achieved by heating the adducts in the substantial absence of moisture or by means of catalysts. Alternatively, the organic compounds containing urethane and/or thiourethane groups and also isocyanate and/or isothiocyanate groups may be converted into a more highly polymerized state by further reaction with a polyisocyanate and/or polyisothiocyanate.

The products of the instant invention may be in the form of bubble-free resinous compositions or highly cellular resinous foams, the character of the products being dependent upon the conditions of manufacture.

For example, if a substantially bubble-free resin is desired, the reaction between the organic compound containing urethane and/or thiourethane groups with a polyisocyanate and/or polyisothiocyanate is desirably carried out in the absence of a catalyst and also moisture. On the other hand, if a cellular product is desired, the reaction is effected in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl or substituted hydroxyl groups and precursors of said compounds. In either case, the products are relatively brittle resins which may be plasticized and rendered more flexible by effecting their preparation in the presence of a non-reactive organic material, and preferably a non-reactive organic liquid which boils at a temperature not lower than 200° C., and preferably not lower than 250° C., at atmospheric pressure.

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As illustrative examples of non-reactive organic liquids and solids which may be used in the practice of this invention, there may be mentioned trichlorobenzene, chlorinated biphenyl, chlorinated 1,3,3-trimethyl-1-phenyldiane, chlorinated 1,3,3,6-tetramethyl-1(4'-methylphenyl)-indane, dimethoxy tetraethylene glycol, diethyl phthalate, dibutyl phthalate, diethyl phthalate, butyl benzoyl benzoate, butyl phthalyl butyl glycolate, N-ethyl-para-toluene sulfonamide, diphenyl ortho-biphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, dibutyl sebacate, dibenzyl sebacate, partially hydrogenated aromatic hydrocarbon liquid mixtures such as disclosed and claimed in Patent 2,364,719, epoxidized safflower oil and petroleum and coal tar oils which boil above 200° C., and preferably above 250° C., at atmospheric pressure. In fact, any organic liquid or solid boiling within the above range which is compatible with the above adducts, the organic compounds containing urethane groups and the final resin may be employed in the practice of the instant invention.

10 The above-described adducts may be preformed and then added to the non-reactive organic liquid or solid and converted to a more highly polymerized state or they may be formed in situ in the organic liquid or solid and then converted to a higher state of polymerization. In either event, the plasticized polymers thus obtained vary from soft resinous gels to hard brittle resins, depending upon the amount and type of components used in their production.

15 For a more complete understanding of the instant invention, reference is made to the following illustrative examples, although it should be clearly understood that the invention is not limited thereto.

EXAMPLE I

Manufacture of Substantially Bubble-Free Gels and Resins

About 11.1 parts of triethanolamine was reacted with about 38.9 parts of m-tolylene diisocyanate in the presence of about 50 parts of chlorinated biphenyl containing 42% chlorine. The resulting mixture consisted of a white solid suspended in a yellow liquid. This liquid was separated and heated in an oven at a temperature of 100° C. for about 12 hours and a hard, clear resin was obtained.

A sample of this resin was held in a Bunsen flame and it burned with a smokey flame without melting but extinguished itself as soon as it was removed.

EXAMPLE II

About 55.5 parts of triethanolamine and about 250 parts of chlorinated biphenyl containing 42% chlorine were mixed thoroughly in a flask and then about 194.5 parts of m-tolylene diisocyanate was added with stirring. During this addition, the reaction temperature was maintained at a value not exceeding 50° C. This resulted in the production of a slurry of a solid material which was separated from the liquid by filtering. A sample of the liquid reaction product was placed in an oven at 100° C. and, after about 18 hours, the liquid solidified. The solubility of this product in various liquids was determined and it was found that the resin did not dissolve in boiling solvents such as water, methanol, acetone, hexane, benzene, carbon tetrachloride and ethyl acetate.

EXAMPLE III

55 About 39.1 parts of diethanolamine and about 250 parts of chlorinated biphenyl containing 42% chlorine was reacted with about 194.5 parts of m-tolylene diisocyanate to form a liquid product containing a relatively small proportion of solid material which was separated by filtering. The liquid product was then heated in an oven at 100° C. until it solidified into a hard, clear resin.

EXAMPLE IV

About 38.9 parts of m-tolylene diisocyanate and about 70 11.1 parts of triethanolamine were reacted together in

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the presence of about 50 parts of nuclear chlorinated isopropylbiphenyl containing about 42% chlorine. The reaction product consisted of a liquid containing a relatively small proportion of solids which were removed by filtration. The liquid portion of the reaction product was heated in an oven at 100° C. for a period of about 24 hours and a soft, yellow resinous gel was obtained.

EXAMPLE V

About 11.1 parts of triethanolamine and about 38.9 parts of m-tolylene diisocyanate were reacted together in the presence of about 50 parts of the following solvents:

- Sample No. 1 Chlorinated biphenyl containing 21% chlorine
- Sample No. 2 Chlorinated biphenyl containing 32% chlorine
- Sample No. 3 Chlorinated biphenyl containing 42% chlorine
- Sample No. 4 Chlorinated biphenyl containing 48% chlorine
- Sample No. 5 Chlorinated biphenyl containing 54% chlorine
- Sample No. 6 Chlorinated biphenyl containing 60% chlorine
- Sample No. 7 Chlorinated naphthalene

On heating to a temperature of 100° C. and for a period of about 20 hours, Samples Nos. 1-5 and 7 formed clear, amber resins whereas Sample No. 6 produced a sticky, opaque resin.

EXAMPLE VI

About 55.5 parts of triethanolamine and about 194.5 parts of m-tolylene diisocyanate were reacted together in the presence of about 250 parts of chlorinated biphenyl containing 42% chlorine. This reaction was carried out at room temperature using chlorinated biphenyl which had been previously saturated with hydrogen chloride gas. This resulted in the production of a liquid containing a relatively small proportion of solids which were removed by filtration. A sample of this liquid product was heated at a temperature of 100° C. for about 3½ hours to form a thick gel and for a total of about 4½ hours to form a very hard and brittle resin which was substantially free of bubbles.

EXAMPLE VII

About 8.3 parts of triethanolamine and about 41.7 parts of p,p'-diisocyanatodiphenylmethane were reacted together in the presence of about 50 parts of chlorinated biphenyl containing about 42% chlorine. The resulting reaction product was placed in a 100° C. oven and heated for about 5 hours. This resulted in the production of a hard, clear, yellow resin similar to that obtained with m-tolylene diisocyanate.

EXAMPLE VIII

About 11.1 parts of triethanolamine was dissolved in about 50 parts of molten biphenyl and to the resulting solution about 38.9 parts of m-tolylene diisocyanate was added. The product obtained as a result of the ensuing reaction was heated for about 24 hours at 100° C. and a hard, clear, light yellow resin was obtained.

EXAMPLE IX

About 10.3 parts of castor oil was reacted with about 4.7 parts of m-tolylene diisocyanate in the presence of chlorinated biphenyl containing 42% chlorine, the reaction taking place at room temperature. The product of this reaction was a clear, viscous liquid which, on heating for about 40 hours at 125° C., yielded a flexible, bubble-free resin.

EXAMPLE X

m-Tolylene diisocyanate and the condensate of about

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6.6 mols of propylene oxide with 1 mol of glycerine were reacted together in a molar ratio of about 3 mols of the diisocyanate to about 1 mol of the condensate, the reaction taking place in the presence of a sufficient amount of chlorinated biphenyl containing 42% chlorine to yield a 50% solution of adduct. On heating for 2½ hours at 140° C., a sample of this solution yielded a tough, rubbery and resinous gel.

EXAMPLE XI

- 10 m-Tolylene diisocyanate containing about .23% of hydrolyzable chlorine was reacted with the following alkylene oxide condensates of glycerine in a molar ratio of about 3 mols of the isocyanate to about 1 mol of the condensate, the reaction taking place in the presence of a sufficient amount of chlorinated biphenyl containing 42% chlorine to yield a 50% solution of the adduct.
- 15 Condensate of about 3.1 mols of propylene oxide with 1 mol of glycerine
- 20 Condensate of about 13.2 mols of propylene oxide with 1 mol of glycerine
- Condensate of about 12 mols of ethylene oxide with 1 mol of glycerine
- 25 Condensate of about 3 mols of ethylene oxide with 1 mol of glycerine

The products of these reactions were all clear, viscous liquids except the solution of adduct prepared from 3.1 mols of propylene oxide with 1 mol of glycerine, which product was a cloudy, viscous liquid. On being heated to 150° C. for 3 hours, 4½ hours, 7½ hours and 4½ hours, respectively, these reaction products formed gels which, on continued heating for a total of 23 hours at the same temperature, produced flexible, bubble-free resins that decreased in flexibility with decreasing molecular weight of the condensate used in the preparation of the adduct.

EXAMPLE XII

- 30 Solutions of the following compositions, when heated for about 23 hours at 125° C., yielded substantially bubble-free products which varied with decreasing amounts of solvent from a soft jelly to a tough, flexible resin.
- 35

	Adduct	Percent by weight of adduct	Percent by weight of chlorinated biphenyl containing 42% chlorine
45			
50	Adduct of about 3 mols of m-tolylene diisocyanate with about 1 mol of the condensate of 13.2 mols of propylene oxide with 1 mol of glycerine.....	20 35 65 80	80 65 35 20
55			

EXAMPLE XIII

- 55 Solutions of the following compositions, when heated for about 23 hours at 125° C., produced substantially bubble-free, brittle resins which increased in hardness as the amount of solvent was decreased.
- 60

	Adduct	Percent by weight of adduct	Percent by weight of chlorinated biphenyl containing 42% chlorine
65			
70	Adduct of 3 mols of m-tolylene diisocyanate with 1 mol of the condensate of 3.1 mols of propylene oxide with 1 mol of glycerine.....	20 35 65 80	80 65 35 20
75			

EXAMPLE XIV

Substantially 3 mols of m-tolylene diisocyanate was re-

acted with the condensation product of about 13.2 mols of propylene oxide with 1 mol of glycerine in the presence of a sufficient amount of the following chlorinated compounds numbered 1-6, inclusive, to yield a 50% solution of the resulting adducts. In the remaining cases, namely, 7-9, inclusive, the condensation product was mixed with similar amounts of the melted chlorinated compound and then reacted with the m-tolylene diisocyanate.

Physical appearance of adduct

(1) Unrefined chlorinated biphenyl containing 48% by weight of chlorine.....	Dark liquid.
(2) Chlorinated biphenyl containing 21% chlorine.....	Clear, viscous liquid.
(3) Chlorinated biphenyl containing 32% chlorine.....	Do.
(4) Refined chlorinated biphenyl containing 48% chlorine.....	Do.
(5) Refined chlorinated biphenyl containing 54% chlorine.....	Do.
(6) Refined chlorinated biphenyl containing 60% chlorine.....	Very viscous, clear liquid.
(7) Chlorinated mixture of 60% biphenyl and 40% distilled high boiler containing 65% chlorine.....	Clear, extremely viscous liquid.
(8) Chlorinated isomeric terphenyl mixture containing 42% chlorine.....	Do.
(9) Chlorinated distilled high boiler containing 60% chlorine.....	Clear solid.

The products obtained as a result of these reactions were heated at a temperature of 125° C. until a gel was formed, whereupon the heating was continued for a total of 13 hours to convert the gel into a resin. The time required to gel the above products and the type of resins formed are indicated in the following table.

Sample No.	Total time required for sample to gel	Type of resin formed
1.....	Greater than 6 hours.....	Dark, flexible, soft, bubble-free resin.
2.....	2½ hours.....	Flexible, bubble-free resin.
3.....	1½ hours.....	Do.
4.....	do.....	Do.
5.....	Greater than 6 hours.....	Soft, flexible, bubble-free resin.
6.....	do.....	Soft, flexible resin with a few bubbles.
7.....	1½ hours.....	Hard, flexible, bubble-free resin.
8.....	2½ hours.....	Flexible, bubble-free resin.
9.....	do.....	Brittle resin with a few bubbles.

EXAMPLE XV

Substantially 3 mols of m-tolylene diisocyanate was reacted with about 1 mol of the condensation product of about 13.2 mols of propylene oxide with 1 mol of glycerine, the reaction taking place in the presence of a sufficient amount of the following organic liquids to form a 50% solution of the adduct having the properties indicated:

Sample No.	Organic liquid	Physical properties of solution of adduct
1.....	Partially hydrogenated aromatic liquid mixture having a specific gravity of about 1.004 at 25° C., a refractive index of about 1.5600 at 25° C. and a boiling range of 340° C. to 390° C. at atmospheric pressure.	Clear, viscous liquid.
2.....	Chlorinated 1,3,3-trimethyl-1-phenylindane.	Do.
3.....	Epoxydized safflower oil.....	Do.
4.....	Tricresyl phosphate.....	Do.
5.....	2-Ethylhexyl diphenyl phosphate.....	Do.
6.....	Butyl phthalyl butyl glycolate.....	Do.
7.....	Dimethoxy tetraethylene glycol.....	Clear liquid.

The above products were heated at a temperature of about 125° C. until they were gelled and then the gels were heated up to a total of 22½ hours to convert them into resins. The time required for the products to gel and the properties of the resins are given in the following table.

	Time required for sample to gel, hrs.	Type of resin formed
5.....	Greater than 6½.....	Flexible resin with some tendency of organic liquid to exude.
2.....	3½.....	Flexible resin.
3.....	1.....	Do.
4.....	5½.....	Do.
5.....	3.....	Do.
6.....	5½.....	Do.
7.....	More than 2½.....	Do.

EXAMPLE XVI

About 3 mols of m-tolylene diisocyanate was reacted with about 1 mol of the condensate of 13.2 mols of propylene oxide with 1 mol of glycerine, the reaction being executed in the presence of a sufficient amount of tricresyl phosphate or chlorinated biphenyl containing 42% chlorine to yield 20%, 50% and 80% solutions of the adduct. A similar reaction was carried out using about 20 mols of m-tolylene diisocyanate and about 1 mol of the condensate of 3.1 mols of propylene oxide with 1 mol of glycerine. The resulting reaction products were further heated to yield resinous polymers plasticized by the solvent employed.

Similar products were also made by adding the above condensates to the following molten chlorinated compounds, reacting m-tolylene diisocyanate with the condensate in the molar ratio indicated above and then heating the resulting products to convert them into plasticized resinous polymers.

- (1) A chlorinated mixture consisting of 60% biphenyl and 40% distilled high boiler containing about 65% chlorine
- (2) A chlorinated isomeric terphenyl mixture containing 42% chlorine
- (3) Chlorinated distilled high boiler containing about 60% chlorine

In order to determine the temperature characteristics of these resins, they were cooled to -12° C. and heated to 200° C. and 300° C. on a Fisher-Johns melting point apparatus. All of these resins were liquid or extremely soft at 300° C. and gave off vapor. At 200° C. very little change in the nature of the resins was noted, but at -12° C., all of these resins were quite brittle.

EXAMPLE XVII

About 8 parts of the condensate of 13.2 mols of propylene oxide with 1 mol of glycerine was reacted with about 7 parts of p,p'-diisocyanatodiphenylmethane which had been pretreated with HCl gas, the reaction being executed in the presence of 15 parts of chlorinated biphenyl containing about 42% chlorine. The product of this reaction was a soft, sticky, gummy, cloudy liquid. A sample of this product was heated at 125° C. for a period of about 15 hours and a clear, flexible resin substantially free of bubbles was obtained.

EXAMPLE XVIII

A mixture of about 15 parts of chlorinated biphenyl containing 42% chlorine and about 15 parts of the adduct of about 3 mols of m-tolylene diisocyanate with about 1 mol of the condensate of 9.2 mols of ethylene oxide with 1 mol of triethanolamine was prepared and then heated at 140° C. for about 25 to 30 minutes. This yielded a clear, tough, resinous product.

EXAMPLE XIX

About 40.7 parts of the condensate of 11.98 mols of ethylene oxide with 1 mol of glycerine was reacted with about 34.3 parts of m-tolylene diisocyanate containing 0.24% hydrolyzable chlorine, the reaction being executed in the presence of about 75 parts of chlorinated biphenyl containing 54% chlorine. The product of this reaction was heated at 110° C. for about 115 hours and a clear resin was obtained. A sample of this resin was held in

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the flame until it was burning well and then it was withdrawn. On being withdrawn, the product did not continue to burn.

EXAMPLE XX

About 244 parts of the condensate of 11.98 mols of ethylene oxide with 1 mol of glycerine was reacted with about 205.3 parts of m-tolylene diisocyanate containing 0.24% of hydrolyzable chlorine, the reaction taking place at room temperature and in the presence of about 450 parts of chlorinated biphenyl containing 42% chlorine. This reaction yielded a product which, on heating at about 110° C. for a period of about 68 hours, produced a completely bubble-free clear, flexible and tough resin.

A sample of the product of the initial reaction was used to impregnate and/or laminate glass cloth with highly satisfactory results. In producing these products, the solution of the initial reaction product was applied to a sheet of cloth and also between two sheets of cloth and then heated to effect polymerization of the adduct.

EXAMPLE XXI

About 6.8 parts of the condensate of 11.98 mols of ethylene oxide with 1 mol of glycerine was reacted with about 8.2 parts of p,p'-diisocyanatodiphenylmethane in the presence of about 15 parts of chlorinated biphenyl containing 42% chlorine, the reaction taking place at room temperature. The isocyanate used in this reaction was pretreated with hydrogen chloride to insure the presence of a trace of HCl. The product of this reaction was a very viscous, sticky liquid which, on heating at a temperature of about 125° C. for about 15 hours, yielded a flexible, clear resin substantially free of bubbles.

EXAMPLE XXII

Manufacture of Resinous Foams

The procedure described in Example X was repeated except that 1% by weight of calcium oxide was added to a sample of the resulting solution of adduct. On heating this sample at 140° C. for 10 minutes, it was converted initially into a gel and finally into a porous resinous foam.

EXAMPLE XXIII

The procedure used in Example XI was repeated using m-tolylene diisocyanate which had been pretreated with hydrogen chloride, and a condensate of about 3 mols of propene oxide with 1 mol of glycerine to form a 50% solution of adduct. A sample of this solution was mixed with about 1% by weight of lead oxide and the resulting mixture heated at 140% C. for about 1½ to 1¾ hours. This resulted in the production of a rubbery, resinous foam.

EXAMPLE XXIV

About 66.2 parts of castor oil was dissolved in about 100 parts of chlorinated biphenyl containing 54% chlorine by heating and to the resulting solution about 33.8 parts of m-tolylene diisocyanate and about 5 parts of N-methylmorpholine were successively added. After the formation of the adduct had been completed, about 1% of N-methylmorpholine and about 0.4% of benzyltrimethylammonium hydroxide were introduced with stirring. The ensuing reaction, which was carried out at room temperature, resulted in the production of a resinous foam. This product was given an additional cure by heating for 15 minutes at about 100° C. and a light colored rubbery foam of substantially uniform cell size was obtained.

EXAMPLE XXV

The preceding example was repeated using hydrogenated instead of natural castor oil. This resulted in the production of a light colored rubbery foam which was slightly firmer than that obtained in the previous example.

The organic compound containing a urethane or thi-

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urethane group or one or more of these groups and an isocyanate and/or an isothiocyanate group is desirably prepared in the presence of a non-reactive organic plasticizer, preferably a non-reactive organic liquid plasticizer, which boils at a temperature of at least 200° C. and preferably at a temperature of at least 250° C. at atmospheric pressure. This yields a solid or a viscous liquid solution of the above organic compound, which is stable for a considerable period of time if stored at room temperature in tightly closed containers. However, if heated or treated in the manner hereinafter described, the solution is converted into a complex resinous polymer plasticized by the above-mentioned plasticizer.

The curing of the solid or viscous liquid solution of the above-mentioned organic compound is effected by heating in the substantial absence of moisture or other foreign materials containing reactive hydrogen atoms. This heating is sufficient to effect a reaction between at least one urethane or thiourethane group and an isocyanate and/or an isothiocyanate group of another molecule containing both types of functional groups. In the event that the organic compound contains only urethane or thiourethane groups, then it is cured by reaction with an added compound which contains at least one isocyanate and/or isothiocyanate group, the curing taking place at a temperature sufficient to bring about a reaction between the functional groups of the two compounds involved.

The curing operation is carried out in the absence or presence of a catalyst and at a temperature varying from room temperature up to about 225° C. or more specifically, from about 60° C. to about 200° C. and within these limits, a temperature of about 100° C. to about 125° C. is preferred.

In the production of cellular products or plastic foam, the curing is effected at room temperature by merely mixing the organic material containing a urethane or a thiourethane group or a solution thereof with a relatively small proportion of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl or substituted hydroxyl groups and precursors of these compounds. The expression "substituted hydroxyl groups" signifies radicals of the formula —OX, in which X is a member selected from the group consisting of aliphatic, cycloaliphatic, aryl, alkaryl, aralkyl and substituted hydrocarbon radicals which may or may not be interrupted by non-reactive hetero atoms such as sulfur and oxygen, etc. For example, these hydrocarbon radicals may be substituted by alkyl, alkoxy, halogen and/or nitro groups. Illustrative examples of preferred catalysts within the group are the oxides or hydroxides of potassium, sodium and calcium; the oxides of magnesium, zinc and lead; the alkali metal salts and particularly the sodium salts of ortho-phenyl phenol, 2,4,5-trichlorophenol and 2,3,4,6-tetrachlorophenol; and benzyltrimethylammonium hydroxide, tetramethylammonium hydroxide, tetramethylphenylammonium hydroxide, tetraethylammonium hydroxide, etc. These catalysts may be used alone or in combination with tertiary organic amines such as N-methylmorpholine, N-ethylmorpholine, triethylamine, tripropylamine, tributylamine, triamylamine, pyridine and quinoline, etc. If desired, the rate of curing may be greatly accelerated by heating the solid or liquid solution to higher temperatures within the limits set forth above.

The curing may be carried out in the absence or presence of moisture or a plasticizer.

In the production of cellular products or plastic foams, the catalyst is employed in an amount varying from about 0.001% to about 5% by weight or more specifically, within the range of about 0.1% to about 3% by weight and within these limits about 0.5% to about 1% is preferred. The percentage by weight is based upon the weight of the total reactants.

In the production of plasticized products in accordance with this invention, the liquid or solid plasticizer is desir-

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ably employed in an amount varying from about 20% to about 80% by weight, basis total weight, and within these limits about 40% to about 60% by weight is preferred. If desired, larger or smaller amounts may be employed in order to affect the desired degree of plasticization.

The plasticized products of the instant invention cannot be produced by first forming the polymerized or cured organic compound containing a urethane or thiourethane group and then incorporating the cured product with the plasticizer. In order to obtain products having satisfactory properties, the organic compound containing the urethane or thiourethane group must be intimately associated with the plasticizer and then polymerized or cured to a higher molecular state. In this operation, the organic compound containing the urethane or thiourethane group may be preformed and then added to the plasticizer or it may be formed in situ.

What I claim is:

1. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a first polymer comprising a condensation product of about 100 parts by weight of propylene oxide and about 7.5 to 10 mole percent based on the propylene oxide of pentaerythritol, and (2) at least about 2 moles based on the amount of said condensation product used of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of the first polymer is formed.

2. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of propylene oxide and about 7.5 to 10 mole percent based on the propylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 4 hydroxyl groups and (2) at least about 1½ moles per mole of condensation product of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

3. The reaction product of (1) a condensate of propylene oxide and a polyhydric alcohol having from 3 to 4 hydroxyl groups, and (2) an organic polyisocyanate, the amount of (2) being in excess of that theoretically required to react with the reactive hydrogens of said condensate.

4. A method for making a polyurethane reaction product which comprises mixing (1) a condensate of propylene oxide and a trihydric alcohol with (2) an organic polyisocyanate in a ratio of greater than one —NCO per reactive hydrogen of said condensate, and reacting the mixture until a second polymer having a chain length greater than that of said condensate is formed.

5. A process for making a reaction product which comprises reacting (1) a condensate of propylene oxide and a polyhydric alcohol having from 3 to 4 hydroxyl groups and (2) a member selected from the group consisting of an organic polyisocyanate and an organic polyisothiocyanate, the amount of (2) being in excess of that theoretically required to react with the reactive hydrogens of said condensate.

6. The process of claim 5 wherein the said condensate is reacted with an organic polyisocyanate.

7. A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) an hydroxy terminated polyether polymer which is a condensation product of propylene oxide and a polyhydric alcohol having less than 7 carbon atoms and having 3 to 4 primary hydroxyl groups, and (2) an organic diisocyanate, in an amount providing a ratio of —NCO groups to the reactive hydrogens of said polyether greater

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than 1 to 1, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether polymer is formed.

8. A process of preparing a polyurethane reaction product comprising the steps of mixing (1) a liquid hydroxyl terminated polyether polymer which is a condensation product of propylene oxide and a polyhydric alcohol of less than 7 carbon atoms and having 3 to 4 hydroxyl groups, and (2) an organic polyisocyanate having 2 to 3 functional isocyanate groups in a ratio of greater than one —NCO per reactive hydrogen of said polyether polymer, and reacting the mixture to form a reaction product having a chain length substantially greater than that of said polyether polymer.

9. A product made according to the process of claim 8.

10. A process of forming a polyurethane comprising the steps of mixing (1) a condensation product of propylene oxide and glycerine, and (2) an organic polyisocyanate in a ratio of greater than one —NCO per reactive hydrogen of said condensation product, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

11. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of propylene oxide and an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 4 hydroxyl groups and (2) an organic diisocyanate in a ratio providing more than one —NCO per reactive hydrogen of said condensation product, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

12. A process of forming a polyurethane reaction product comprising the steps of mixing a first polymer comprising a condensation product of propylene oxide and an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 4 hydroxyl groups, and at least about 2 moles, based on the amount of said condensation product, of an organic diisocyanate and reacting the mixture until a second polymer having a chain length substantially greater than the first polymer is formed.

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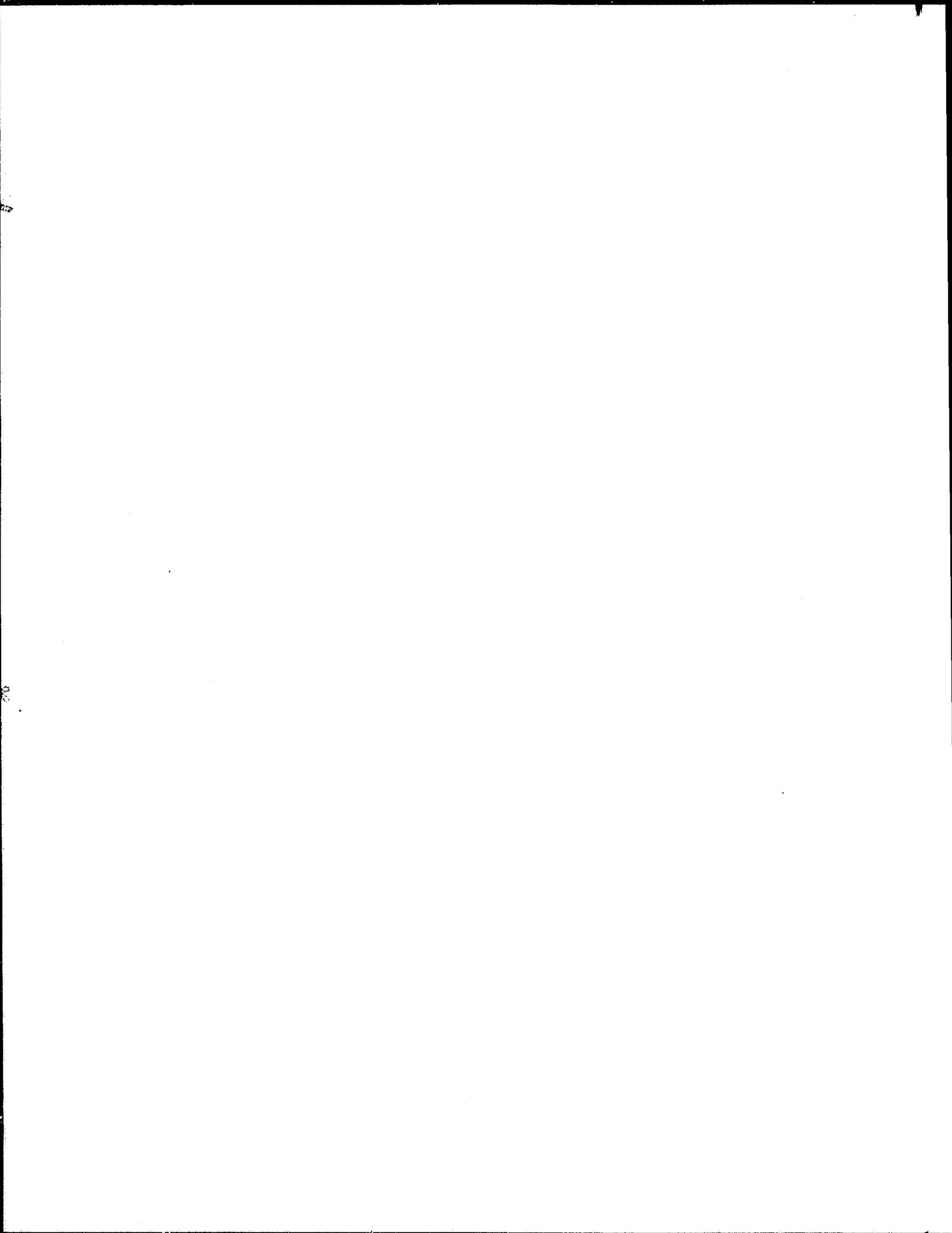
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Certified copy of file history of Patent No. 3,102,875

Pages 507a to 683a



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PATENT

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SEP 10 1968

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Assignee: The Goodyear Tire & Rubber Company, Akron, Ohio
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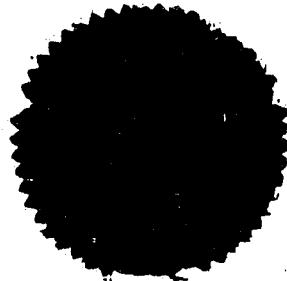
NOVEL RUBBER COMPOSITIONS AND METHOD OF PRODUCING SAME

Characteristics, Function, Product, and Method for Producing Same

ORIGINAL

APPLICATION FILED COMPLETE AUG 7 1968

(including Specification,)



Heiss L. 41
Aug 10 1968
1-17-68
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JAMES H. SAUNDERS AND HERBERT L. HEISS # 3

HERBERT L. HEISS

ANNISTON
ALABAMA

ALABAMA

Invention

Total Aromatic Compositions and Methods of Preparing Same Benzene Reaction Product And Method For Making It

ORIGINAL

BING 2 1963

APPLICATION FILED COMPLETE

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Examined and passed for Issue DEC 11 1962 by Dr. J. G. L. Johnson
Action of Assurance DEC 11 1962

DEPARTMENT OF STATE

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MONSANTO CHEMICAL COMPANY



ANNISTON, ALABAMA

PHONE: ANNISTON 1800

August 3, 1953

Hon. Commissioner of Patents
Washington 25, D. C.

Re: Application of James H. Saunders et al
A-142 NOVEL RESINOUS COMPOSITIONS AND
METHOD OF PRODUCING SAME

Dear Sir:

I am enclosing herewith the above-entitled application for filing in
the Patent Office.

A check in the amount of \$30.00 is also enclosed to cover the filing
fee.

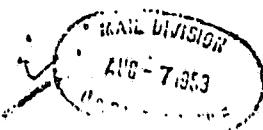
Yours very truly,

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Elmer P. Rucker

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NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAME

The present invention relates to a new series of resins, compositions of matter containing same and to the method of preparing such products.

5 The products of this invention are suitable for casting or pouring into intricate forms or crevices and are adapted for use in numerous applications, for example, as adhesives, protective coatings, components of insulating varnishes, impregnants for fibrous material to impart water resistance, flame resistance and improved hand thereto; as insulating and dielectric elements in transformers, capacitors, electrical terminals or bushings, cables or other electric devices; and as foamed-in-place resins. The products of relatively low molecular weight, that is, those derived from monoamines, monohydroxy compounds or monorcarbons, find use as plasticizers for vinyl resins and numerous other plastic materials.

In accordance with the instant invention, the new products are prepared by reacting an organic compound containing at least one urethane or thiourethane group with a compound of the general formula: R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCO, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, the second-mentioned reactant being employed in an amount sufficient to react with the urethane and/or thiourethane groups of the first-mentioned reactant. More specifically, the new products are prepared by reacting an organic compound containing a plurality of urethane and/or thiourethane groups with a compound of the above general formula wherein n is an integer having a value of at least 2, the second-mentioned reactant being employed in an amount sufficient to react with at least two urethane groups or one urethane and one thiourethane group of the first-mentioned reactant.

The organic compounds containing at least one urethane or thiourethane group and preferably a plurality of these groups may be prepared in any suitable manner. For example, compounds containing urethane groups are prepared by reacting an organic hydroxy compound, preferably an organic polyhydroxy compound, with polyisocyanates, carboxyl halides such as carbamyl chloride, urea or substituted ureas; or by reacting mono- or polyamines with halocarbonates such as chlorocarbonates. Compounds containing thiourethane groups are prepared by reacting polyisocyanates with mercaptans or polymercapto compounds.

As illustrative examples of suitable hydroxy compounds for use in the production of organic compounds containing urethane groups, there may be mentioned methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, amyl alcohol, hexyl alcohol, octyl alcohol, decyl alcohol, lauryl alcohol, allyl alcohol, cetyl alcohol, tridecyl alcohol, stearyl alcohol, methyl ricinoleate, ethyl lactate, diglycerides, monoesters of glycols, phenols, substituted phenols, alkylene oxide condensates of these hydroxy compounds, ethylene glycol, propylene glycol, butylene glycol-2,3 butylene glycol-1,3, 2-methyl pentanediol-2,4, 2-ethylhexane-diol-1,3, hexamethylene glycol, styrene glycol, *M*-phenyldiethanolamine, catechol, resorcinol, 2,2-bis(4-hydroxyphenyl)propane, *p,p'*-dihydroxybiphenyl, decamethylene glycol; polyglycols (ether glycols) such as polyethylene glycols, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycols 200, 400 and 600; polypropylene glycols, dipropylene glycol, tripropylene glycol, polypropylene glycols 400, 750, 1200 and 2000; Carbowaxes 1000, 1000 W, 1500; monoethers of trihydroxy compounds such as glycercyl- α -allyl ether, glycercyl- α -phenyl ether, glycercyl- α -isopropyl ether; hydroxy esters such as an ester prepared from 1 mol of dibasic acid and 2 mols of a glycol or polyglycol, a polyester prepared so that the molar ratio of glycol or polyglycol to the dibasic acid is between 2 and 1, an ester prepared from 1 mol of a dimer acid and 2 mols of a glycol or polyglycol, an ester prepared from a hydroxy acid and a glycol or polyglycol so that the molar ratio of the glycol or

polyglycol to the hydroxy acid is between 0.5 and 1 and an ester prepared from 1 mol of a trihydroxy compound and 1 mol of a monobasic acid, such as the monoglyceride of aleostearic acid; trihydroxy compounds such as glycerine, triethanolamine, pyrogallol, phloroglucinol, etc., alkylene oxide condensates of glycerine, triethanolamine, pyrogallol, phloroglucinol, etc.; monoethers of tetrahydroxy compounds; esters prepared from hydroxy acid and a trihydroxy compound so that the molar ratio of the latter to the former is between 0.33 and 1, such as glycerine triricinolene, esters prepared from 1 mol of a monobasic acid and 1 mol of a tetrahydroxy compound; tetrahydroxy compounds such as pentaerythritol, etc., alkylene oxide condensates of pentaerythritol, etc., esters prepared from 1 mol of a dibasic acid and 2 mols of a trihydroxy compound; pentahydroxy compounds, such as arabitol, xylitol, etc.; hexahydroxy compounds such as sorbitol, ducitol, and mannitol, etc.

Examples of suitable compounds which may be reacted with polyisocyanates to form thiourethanes are methyl mercaptan, ethyl mercaptan, butyl mercaptan, octyl mercaptan, cyclohexyl mercaptan, octadecyl mercaptan, allyl mercaptan, phenyl mercaptan, tolyl mercaptan, α -naphthyl mercaptan, dimercaptoethane, 1,2,3-trimercaptopropane, 1,2,3-trimercaptobutane, 1,5-dimercapto-3-(mercaptomethyl)pentane, 1,6-dimercaptohexane, 1,10-dimercaptodecane, 1,6-dimercapto-3-methylhexane, 1,4-dimercaptobenzene, dimercaptovinylene, and polyvinyl mercaptan.

Illustrative examples of suitable isocyanates, isothiocyanates, carbamyl chlorides, and ureas which may be employed in the production of organic compounds containing urethane or thiourethane groups are ethyl, 25 methyl, propyl, butyl, amyl, octyl, decyl, dodecyl, hexadecyl, octadecyl, allyl, isobutyl, isoamyl, cyclohexyl, phenyl, p -tolyl, p -chlorophenyl, p -chlorophenyl and α -naphthyl isocyanates, etc.; ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, etc.; and the corresponding diisothiocyanates; alkylene diisocyanates and diisothiocyanates, such as propylene-1,2-diisocyanate,

butylene-1,2-diisocyanate, butylene-1,3-diisocyanate, butylene-2,3-diisocyanate, and butylene-1,3-diisothiocyanate; alkylidene diisocyanates and diisothiocyanates, such as ethylidene diisocyanate, butylidene diisocyanate and ethylidene diisothiocyanate; cycloalkylene diisocyanates and diisothiocyanates, such as cyclopentylene-1,3-diisocyanate, cyclohexylene-1,2-diisocyanate, cyclohexylene-1,3-diisocyanate, cyclohexylene-1,4-diisocyanate, and cyclohexylene-1,3-diisothiocyanate; cycloalkylidene diisocyanates and diisothiocyanates, such as cyclopentylidene diisocyanate, cyclohexylidene diisocyanate and cyclohexylidene diisothiocyanate; aromatic diisocyanates and diisothiocyanates, such as *p*-phenylene diisocyanate, *p*-phenylene diisocyanate, 1-methyl-2,4-phenylene diisocyanate, naphthylene-1,4-diisocyanate, diphenylene-4,4'-diisocyanate or *p*-phenylene diisothiocyanate; aliphatic-aromatic diisocyanates or diisothiocyanates, such as xylylene-1,4-diisocyanate, xylylene-1,3-diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-diphenylpropane diisocyanate or xylylene-1,4-diisothiocyanate; methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, phenyl, cyclohexyl, *p*-chlorophenyl carboxyl chlorides; *p*-phenylene, *p*-phenylene, 2,4-toluene, 4,4'-mxylene bis-carboxyl chlorides; urea, methylurea, ethylurea, butylurea, phenylurea, *n*-naphthylurea, cyclohexylurea, *p*-dimethylurea, *p*-dicyclohexylurea, *p*-diphenylurea, 1,3-methyltetrahydron and 1,3-ethylphenylurea, etc.

Examples of amines which may be used in the preparation of organic compounds containing urethane groups are: methyl, ethyl, butyl, octyl, cyclohexyl, octadecyl, allyl amines, aniline, *p*-toluidine, substituted anilines and *n*-naphthylamine; ethylene diamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine, octamethylene diamine, decamethylene diamine, dodecamethylene diamine, *N,N'*-dimethyl decamethylene diamine, *N,N'*-dibenzyl hexamethylene diamine, cyclohexylens-1,4-diamine, arche-phenylene diamine, *p*-phenylene diamine, *p*-phenylene diamine, benzidine, naphthalene-1,4-diamine, γ,γ' -diamino dibutyl oxide, γ,γ' -diamine dibutyl sulfide, diisobutene triamine and triethylene tetramine, etc.

As typical examples of halocarbonates which may be reacted with amines to form organic compounds containing urethane groups, there may be mentioned methyl, ethyl, propyl, isopropyl, butyl, cyclohexyl, phenyl, p-tolyl and p-chlorophenyl chlorocarbonates and butylene-1,4- and hexylene-1,6- bis-chlorocarbonates, etc.

The organic compounds containing urethane and/or thiourethane groups used in the practice of the instant invention are preferably prepared by reacting an organic compound of the general formula: R(NCX)_n with an organic polyhydroxy and/or polymercapto compound in the proportions providing a ratio of -NCX groups to active hydrogen atoms which is greater than 1:1 but is desirably within the range of 1.1:1 to n:1. More specifically, these reactants are employed in the proportions providing a ratio of -NCX groups to active hydrogen atoms which falls in the range of about 1.3:1 or 1.5:1 to about n:1 and preferably within the range of about 2:1 to about n:1. The products obtained by this reaction are adducts which contain urethane and/or thiourethane groups and also free isocyanate and/or isothiocyanate groups. Therefore, these products can be converted into more highly polymerized products by bringing out a reaction between the isocyanate and/or isothiocyanate groups of one molecule with the urethane and/or thiourethane groups of the same or another molecule. This is achieved by heating the adducts in the substantial absence of moisture or by means of catalysts. Alternatively, the organic compounds containing urethane and/or thiourethane groups and also isocyanate and/or isothiocyanate groups may be converted into a more highly polymerized state by further reaction with a polyisocyanate and/or polyisothiocyanate.

The products of the instant invention may be in the form of bubble-free resinous compositions or highly cellular resinous foams, the character of the products being dependent upon the conditions of manufacture.

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For example, if a substantially bubble-free resin is desired, the reaction between the organic compound containing urethane and/or thiourethane groups with a polyisocyanate and/or polyisothiocyanate is desirably carried out in the absence of a catalyst and also moisture. On the other hand, if a cellular product is desired, the reaction is effected in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl or substituted hydroxyl groups and precursors of said compounds. In either case, the products are relatively brittle resins which may be plasticized and rendered more flexible by effecting their preparation in the presence of a non-reactive organic material, and preferably a non-reactive organic liquid which boils at a temperature not lower than 200°C., and preferably not lower than 250°C., at atmospheric pressure.

As illustrative examples of non-reactive organic liquids and solids which may be used in the practice of this invention, there may be mentioned trichlorobenzene, chlorinated biphenyl, chlorinated 1,3,3-trimethyl-1-phenylindane, chlorinated 1,3,3,6-tetramethyl-1(4'-methyl-phenyl)indane, dimethoxy tetraethylene glycol, diethyl phthalate, di-butyl phthalate, diethyl phthalate, butyl benzoyl benzoate, butyl phthalyl butyl glycolate, N-ethyl-para-toluene sulfonamide, diphenyl ortho-biphenyl phosphate, tricrenyl phosphate, 2-ethylhexyl diphenyl phosphate, dibutyl sebacate, dibenzyl sebacate, partially hydrogenated aromatic hydrocarbon liquid mixtures such as disclosed and claimed in patent 2,364,719, epoxidized safflower oil and petroleum and coal tar oils which boil above 200°C., and preferably above 250°C., at atmospheric pressure. In fact, any organic liquid or solid boiling within the above range which is compatible with the above adducts, the organic compounds containing urethane groups and the final resin may be employed in the practice of the instant invention.

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The above-described adducts may be preformed and then added to the non-reactive organic liquid or solid and converted to a more highly polymerized state or they may be formed in situ in the organic liquid or solid and then converted to a higher state of polymerization. In either event, the plasticized polymers thus obtained vary from soft resinous gels to hard brittle resins, depending upon the amount and type of components used in their production.

For a more complete understanding of the instant invention, reference is made to the following illustrative examples, although it should be clearly understood that the invention is not limited thereto.

Example I AF 111-214

Manufacture of Substantially Bubble-Free Gels and Resins

About 11.1 parts of triethanolamine was reacted with about 38.9 parts of μ -tolylene diisocyanate in the presence of about 50 parts of chlorinated biphenyl containing 42% chlorine. The resulting mixture consisted of a white solid suspended in a yellow liquid. This liquid was separated and heated in an oven at a temperature of 100°C. for about 12 hours and a hard, clear resin was obtained.

A sample of this resin was held in a Bunsen flame and it burned with a smoky flame without melting but extinguished itself as soon as it was removed.

Example II AF 111-214

About 55.5 parts of triethanolamine and about 250 parts of chlorinated biphenyl containing 42% chlorine were mixed thoroughly in a flask and then about 194.5 parts of μ -tolylene diisocyanate was added with stirring. During this addition, the reaction temperature was maintained at a value not exceeding 50°C. This resulted in the production of a slurry of a solid material which was separated from the liquid by filtering. A sample of the liquid reaction product was placed in an oven at

100°C. and, after about 18 hours, the liquid solidified. The solubility of this product in various liquids was determined and it was found that the resin did not dissolve in boiling solvents such as water, methanol, acetone, hexane, benzene, carbon tetrachloride and ethyl acetate.

5 Example III) 1/166 5/ps

A slurry containing about 39.1 parts of diethanolamine and about 250 parts of chlorinated biphenyl containing 42% chlorine was reacted with about 194.5 parts of *m*-tolylene diisocyanate to form a liquid product containing a relatively small proportion of solid material which was separated by filtering. The liquid product was then heated in an oven at 100°C. until it solidified into a hard, clear resin.

15 Example IV

About 38.9 parts of *m*-tolylene diisocyanate and about 11.1 parts of triethanolamine were reacted together in the presence of about 50 parts of nuclear chlorinated isopropylbiphenyl containing about 42% chlorine. The reaction product consisted of a liquid containing a relatively small proportion of solids which were removed by filtration. The liquid portion of the reaction product was heated in an oven at 100°C. for a period of about 24 hours and a soft, yellow resinous gel was obtained.

20 Example V

About 11.1 parts of triethanolamine and about 38.9 parts of *p*-tolylene diisocyanate were reacted together in the presence of about 50 parts of the following solvents:

- 25 Sample No. 1 Chlorinated biphenyl containing 21% chlorine
 Sample No. 2 Chlorinated biphenyl containing 32% chlorine
 Sample No. 3 Chlorinated biphenyl containing 42% chlorine
 Sample No. 4 Chlorinated biphenyl containing 48% chlorine

Sample No. 5 Chlorinated biphenyl containing 54% chlorine

Sample No. 6 Chlorinated biphenyl containing 60% chlorine

Sample No. 7 Chlorinated naphthalene

On heating to a temperature of 100°C. and for a period of
about 20 hours, Sample Nos. 1-5 and 7 formed clear, amber resins whereas
Sample No. 6 produced a sticky, opaque resin.

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Example VI) *true. caps*

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About 55.5 parts of triethanolamine and about 194.5 parts of
m-tolylene diisocyanate were reacted together in the presence of about
250 parts of chlorinated biphenyl containing 42% chlorine. This reaction
was carried out at room temperature using chlorinated biphenyl which had
been previously saturated with hydrogen chloride gas. This resulted in
the production of a liquid containing a relatively small proportion of
solids which were removed by filtration. A sample of this liquid pro-
duct was heated at a temperature of 100°C. for about 3 1/4 hours to form
a thick gel and for a total of about 4 1/4 hours to form a very hard and
brittle resin which was substantially free of bubbles.

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Example VII

About 8.3 parts of triethanolamine and about 41.7 parts of
p,p'-diisocyanatodiphenylmethane were reacted together in the presence
of about 50 parts of chlorinated biphenyl containing about 42% chlorine.
The resulting reaction product was placed in a 100°C. oven and heated
for about 5 hours. This resulted in the production of a hard, clear,
yellow resin similar to that obtained with *m*-tolylene diisocyanate.



Example VIII) U.S.C. 64(2)

About 11.1 parts of triethanolamine was dissolved in about 50 parts of molten biphenyl and to the resulting solution about 39.9 parts of μ -tolylene diisocyanate was added. The product obtained as a result of the ensuing reaction was heated for about 24 hours at 100°C., and a hard, clear, light yellow resin was obtained.

Example IX

About 10.3 parts of castor oil was reacted with about 4.7 parts of μ -tolylene diisocyanate in the presence of chlorinated biphenyl containing 42% chlorine, the reaction taking place at room temperature. The product of this reaction was a clear, viscous liquid which, on heating for about 40 hours at 125°C., yielded a flexible, bubble-free resin.

Example X

μ -Tolylene diisocyanate and the condensate of about 6.6 mols of propylene oxide with 1 mol of glycerine were reacted together in a molar ratio of about 3 mols of the diisocyanate to about 1 mol of the condensate, the reaction taking place in the presence of a sufficient amount of chlorinated biphenyl containing 42% chlorine to yield a 50% solution of adduct. On heating for 2 1/4 hours at 140°C., a sample of this solution yielded a tough, rubbery and resinous gel.

Example XI

μ -Tolylene diisocyanate containing about .23% of hydrolyzable chlorine was reacted with the following alkylene oxide condensates of glycerine in a molar ratio of about 3 mols of the isocyanate to about 1 mol of the condensate, the reaction taking place in the presence of sufficient amount of chlorinated biphenyl containing 42% chlorine to yield a 50% solution of the adduct.

- b41-2*
- ✓✓✓✓*
- ✓*
- Condensate of about 3.1 mols of propylene oxide
with 1 mol of glycerine
- Condensate of about 13.2 mols of propylene oxide
with 1 mol of glycerine
- Condensate of about 12 mols of ethylene oxide with
1 mol of glycerine
- Condensate of about 3 mols of ethylene oxide with
1 mol of glycerine

The products of these reactions were all clear, viscous liquids
 10 except the solution of adduct prepared from 3.1 mols of propylene oxide
with 1 mol of glycerine, which product was a cloudy, viscous liquid. On
being heated to 150°C. for 3 hours, 4 3/4 hours, 7 1/2 hours and 4 3/4
hours, respectively, these reaction products formed gels which, on con-
 15 tinued heating for a total of 23 hours at the same temperature, produced
flexible, bubble-free resins that decreased in flexibility with decreas-
ing molecular weight of the condensate used in the preparation of the
adduct.

Example XIII) 1/14/64

Solutions of the following compositions, when heated for about
 20 23 hours at 125°C., yielded substantially bubble-free products which
varied with decreasing amounts of solvent from a soft jelly to a tough,
flexible resin.

25	Adduct	By Weight Of	
		By Weight Of Adduct	Chlorinated Diphenyl Containing 42% Chlorine
<i>✓✓✓✓</i>	Adduct of about 3 mols of m-tolylene diisocyanate with about 1 mol of the condensate of 13.2 mols of propylene oxide with 1 mol of glycerine	20	80
<i>364</i>	<i>Do</i> _____	35	65
	<i>Do</i> _____	65	35
	<i>Do</i> _____	80	20

Example XXXV) Note Crys

Solutions of the following compositions, when heated for about 23 hours at 125°C., produced substantially bubble-free, brittle resins which increased in hardness as the amount of solvent was decreased.

	Adduct	% by weight of adduct	% by weight of chlorinated biphenyl containing 42% chlorine
6	Adduct of 3 mols of μ -tolylene diisocyanate with 1 mol of the condensate of 3.1 mols of propylene oxide with 1 mol of glycerine	20	80
10	D ₁	35	65
13	D ₂	65	35
	D ₃	80	20

Example XIV, Note Crys

Substantially 3 mols of μ -tolylene diisocyanate was reacted with the condensation product of about 13.2 mols of propylene oxide with 1 mol of glycerine in the presence of a sufficient amount of the following chlorinated compounds numbered 1-6, inclusive, to yield a 50% solution of the resulting adducts. In the remaining cases, namely, 7-9, inclusive, the condensation product was mixed with similar amounts of the melted chlorinated compound and then reacted with the μ -tolylene diisocyanate.

		Physical Appearance of Adduct
6	(1) Unrefined chlorinated biphenyl containing 40% by weight of chlorine	Dark liquid
7	(2) Chlorinated biphenyl containing 21% chlorine	Clear, viscous liquid
8	(3) Chlorinated biphenyl containing 32% chlorine	D ₁
9	(4) Refined chlorinated biphenyl containing 48% chlorine	D ₂

641-2 6/4	(5) Refined chlorinated biphenyl containing 54% chlorine	<u>11 D₁₀</u> Clear, viscous liquid
5	(6) Refined chlorinated biphenyl containing 60% chlorine	Very viscous, clear liquid
10	(7) Chlorinated mixture of 60% biphenyl and 40% distilled high boiler containing 65% chlorine	Clear, extremely viscous liquid
	(8) Chlorinated isomeric terphenyl mixture containing 42% chlorine	<u>11 D₁₀</u> Clear, extremely viscous liquid
15	(9) Chlorinated distilled high boiler containing 60% chlorine	Clear solid

The products obtained as a result of these reactions were heated at a temperature of 125°C. until a gel was formed, whereupon the heating was continued for a total of 13 hours to convert the gel into a resin. The time required to gel the above products and the type of resins formed are indicated in the following table.

Sample No.	Total Time Required For Sample to Gel	Type of Resin Formed
20	1 - Greater than 6 hours	Dark, flexible, soft, bubble-free resin.
	2 1/2 hours	Flexible, bubble-free resin.
	3 1/2 hours	Flexible, bubble-free resin. <u>11 D₁₀</u>
	4 - 1 1/2 hours	Flexible, bubble-free resin. <u>D₁₀</u>
25	5 - Greater than 6 hours	Soft, flexible, bubble-free resin.
30	6 - Greater than 6 hours	Soft, flexible resin with a few bubbles.
	7 - 1 1/2 hours	Hard, flexible, bubble-free resin.
	8 - 2 1/2 hours	Flexible, bubble-free resin.
	9 - 2 1/2 hours	Brittle resin with a few bubbles.

Example IV/1111-41-p1

Substantially 3 moles of m-tolylene diisocyanate was reacted with about 1 mol of the condensation product of about 13.2 moles of propylene oxide with 1 mol of glycerine, the reaction taking place in the presence

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of a sufficient amount of the following organic liquids to form a 50% solution of the adduct having the properties indicated:

Sample No.	Organic Liquid	Physical Properties of Solution of Adduct
5 1	Partially hydrogenated aromatic liquid mixture having a specific gravity of about 1.004 at 25°C., a refractive index of about 1.5600 at 25°C. and a boiling range of 340°C. to 390°C. at atmospheric pressure.	Clear, viscous liquid.
10 2	Chlorinated 1:3:5-trimethyl-1-phenyl-indane.	<input checked="" type="checkbox"/> Do. "
3	Epoxydized safflower oil	" Do. "
4	Tricrearyl phosphate	" Do. "
5	2-ethylhexyl diphenyl phosphate	" Do. "
6	Dimethyl phthalyl butyl glycolate	" Do. "
7	"-octoxy tetraethylene glycol	Clear liquid.

The above products were heated at a temperature of about 125°C.

until they were gelled and then the gels were heated up to a total of 22 1/2 hours to convert them into resins. The time required for the products to gel and the properties of the resins are given in the following table.

	Time Required For Sample to Gel, Hrs.	Type of Resin Formed
25 1	Greater than 6 1/2	Flexible resin with some tendency of organic liquid to exude.
2	3 1/2	Flexible resin,
3	1	<input checked="" type="checkbox"/> Do.
4	5 1/2	" Do.
30 5	3	" Do.
6	5 1/2	" Do.
7	More than 2 1/2	" Do.

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Example XVI) 1/2024 - Clps

About 3 moles of μ -tolylene diisocyanate was reacted with about 1 mol of the condensate of 13.2 moles of propylene oxide with 1 mol of glycerine, the reaction being executed in the presence of a sufficient amount of tricresyl phosphate or chlorinated biphenyl containing 42% chlorine to yield 20%, 50% and 60% solutions of the adduct. A similar reaction was carried out using about 3 moles of μ -tolylene diisocyanate and about 1 mol of the condensate of 3.1 moles of propylene oxide with 1 mol of glycerine. The resulting reaction products were further heated to yield resinous polymers plasticized by the solvent employed.

Similar products were also made by adding the above condensates to the following molten chlorinated compounds, reacting μ -tolylene diisocyanate with the condensate in the molar ratio indicated above and then heating the resulting products to convert them into plasticized resinous polymers.

- l. 1/2024*
- (1) A chlorinated mixture consisting of 60% biphenyl and 40% distilled high boiler containing about 42% chlorine
 - (2) A chlorinated isomeric terphenyl mixture containing 42% chlorine
 - (3) Chlorinated distilled high boiler containing about 60% chlorine

In order to determine the temperature characteristics of these resins, they were cooled to -12°C . and heated to 200°C . and 300°C . on a Fisher-Johns melting point apparatus. All of these resins were liquid or extremely soft at 300°C . and gave off vapor. At 200°C . very little change in the nature of the resins was noted, but at -12°C ., all of these resins were quite brittle.

Example XVII) 1/2024 - Clps

About 8 parts of the condensate of 13.2 moles of propylene oxide with 1 mol of glycerine was reacted with about 7 parts of p,p' -diisocyanatediphenylmethane which had been pretreated with HCl gas, the

reaction being executed in the presence of 15 parts of chlorinated biphenyl containing about 42% chlorine. The product of this reaction was a soft, sticky, gummy, cloudy liquid. A sample of this product was heated at 125°C. for a period of about 15 hours and a clear, flexible resin substantially free of bubbles was obtained.

Example XVIII) RUE - C475

A mixture of about 15 parts of chlorinated biphenyl containing 42% chlorine and about 15 parts of the adduct of about 3 mol of μ -tolylene diisocyanate with about 1 mol of the condensate of 9.2 mol of ethylene oxide with 1 mol of triethanolamine was prepared and then heated at 140°C. for about 25 to 30 minutes. This yielded a clear, tough, resinous product.

Example XIX

About 49.7 parts of the condensate of 11.98 mol of ethylene oxide with 1 mol of glycerine was reacted with about 34.3 parts of μ -tolylene diisocyanate containing 0.24% hydrolyzable chlorine, the reaction being executed in the presence of about 75 parts of chlorinated biphenyl containing 54% chlorine. The product of this reaction was heated at 110°C. for about 115 hours and a clear resin was obtained. A sample of this resin was held in the flame until it was burning well and then it was withdrawn. On being withdrawn, the product did not continue to burn.

Example XX

About 244 parts of the condensate of 11.98 mol of ethylene oxide with 1 mol of glycerine was reacted with about 205.3 parts of μ -tolylene diisocyanate containing 0.24% of hydrolyzable chlorine, the reaction taking place at room temperature and in the presence of about 450 parts of chlorinated biphenyl containing 42% chlorine. This reaction yielded a product which, on heating at about 110°C. for a period

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of about 4^{1/2} hours, produced a completely bubble-free, clear, flexible and tough resin.

A sample of the product of the initial reaction was used to impregnate and/or laminate glass cloth with highly satisfactory results. In producing these products, the solution of the initial reaction product was applied to a sheet of cloth and also between two sheets of cloth and then heated to effect polymerization of the adduct.

Example XXX) 11/26 - C/A/p.1

About 6.8 parts of the condensate of 11.98 mols of ethylene oxide with 1 mol of glycerine was reacted with about 8.2 parts of p,p'-diisocyanatediphenylmethane in the presence of about 15 parts of chlorinated biphenyl containing 42% chlorine, the reaction taking place at room temperature. The isocyanate used in this reaction was pretreated with hydrogen chloride to insure the presence of a trace of HCl. The product of this reaction was a very viscous, sticky liquid which, on heating at a temperature of about 125°C. for about 15 hours, yielded a flexible, clear resin substantially free of bubbles.

Example XXXI) 11/26 - C/A/p.2

Manufacture of Resinous Foams *Lifc*

The procedure described in Example I was repeated except that 15 by weight of calcium oxide was added to a sample of the resulting solution of adduct. On heating this sample at 140°C. for 10 minutes, it was converted initially into a gel and finally into a porous resinous foam.

Example XXXII)

The procedure used in Example II was repeated using α -tolylene diisocyanate which had been pretreated with hydrogen chloride, and a condensate of about 3 mols of propane oxide with 1 mol of glycerine to form a 50% solution of adduct. A sample of this solution was mixed with about 15 by weight of lead oxide and the resulting mixture heated at 140°C. for about 1 1/4 to 1 3/4 hours. This resulted in the production of a rubbery, resinous foam.

Example XXIV

About 66.2 parts of castor oil was dissolved in about 100 parts of chlorinated biphenyl containing 54% chlorine by heating and to the resulting solution about 33.8 parts of γ -tolylene diisocyanate and about 5 parts of N-methylmorpholine were successively added. After the formation of the adduct had been completed, about 1% of N-methylmorpholine and about 0.4% of benzyltrimethylammonium hydroxide were introduced with stirring. The ensuing reaction, which was carried out at room temperature, resulted in the production of a resinous foam. This product was given an additional cure by heating for 15 minutes at about 100°C. and a light colored rubbery foam of substantially uniform cell size was obtained.

Example XXV

The preceding example was repeated using hydrogenated instead of natural castor oil. This resulted in the production of a light colored rubbery foam which was slightly firmer than that obtained in the previous example.

The organic compound containing a urethane or thiourethane group or one or more of these groups and an isocyanate and/or an isothiocyanate group is desirably prepared in the presence of a non-reactive organic plasticizer, preferably a non-reactive organic liquid plasticizer, which boils at a temperature of at least 200°C. and preferably at a temperature of at least 250°C. at atmospheric pressure. This yields a solid or a viscous liquid solution of the above organic compound, which is stable for a considerable period of time if stored at room temperature in tightly closed containers. However, if heated or treated in the manner herein-after described, the solution is converted into a complex resinous polymer plasticized by the above-mentioned plasticizer.

5 The curing of the solid or viscous liquid solution of the above-mentioned organic compound is effected by heating in the substantial absence of moisture or other foreign materials containing reactive hydrogen atoms. This heating is sufficient to effect a reaction between at least one urethane or thiourethane group and an isocyanate and/or an isothiocyanate group of another molecule containing both types of functional groups. In the event that the organic compound contains only urethane or thiourethane groups, then it is cured by reaction with an added compound which contains at least one isocyanate and/or isothiocyanate group, the curing taking place at a temperature sufficient to bring about a reaction between the functional groups of the two compounds involved.

10 The curing operation is carried out in the absence or presence of a catalyst and at a temperature varying from room temperature up to about 225°C. or more specifically, from about 60°C. to about 200°C. and within these limits, a temperature of about 100°C. to about 125°C. is preferred.

15 In the production of cellular products or plastic foam, the curing is effected at room temperature by merely mixing the organic material containing a urethane or a thiourethane group or a solution thereof with a relatively small proportion of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl or substituted hydroxyl groups and precursors of these compounds. The expression "substituted hydroxyl groups" signifies radicals of the formula $\text{R}_1\text{R}_2\text{R}_3\text{O}^\bullet\text{X}$, in which X is a member selected from the group consisting of aliphatic, cycloaliphatic, aryl, alkaryl, aralkyl and substituted hydrocarbon radicals which may or may not be interrupted by non-reactive hetero atoms such as sulfur and oxygen, etc. For example, these hydrocarbon radicals may be substituted by alkyl, alkoxy, halogen and/or nitro

groups. Illustrative examples of preferred catalysts within the group are the oxides or hydroxides of potassium, sodium and calcium; the oxides of magnesium, zinc and lead; the alkali metal salts and particularly the sodium salts of ortho-phenyl phenol, 2,4,5-trichlorophenol and 2,3,4,6-tetrachlorophenol; and benzyltrimethylammonium hydroxide, tetramethylammonium hydroxide, tetramethylphenylammonium hydroxide, tetraethylammonium hydroxide, etc. These catalysts may be used alone or in combination with tertiary organic amines such as N-methylmorpholine, N-ethylmorpholine, triethylamine, tripropylamine, tributylamine, trimylamine, pyridine and quinoline, etc. If desired, the rate of curing may be greatly accelerated by heating the solid or liquid solution to higher temperatures within the limits set forth above. The curing may be carried out in the absence or presence of moisture or a plasticizer.

In the production of cellular products or plastic foams, the catalyst is employed in an amount varying from about 0.001% to about 5% by weight or more specifically, within the range of about 0.1% to about 3% by weight and within these limits about 0.5% to about 1% is preferred. The percentage by weight is based upon the weight of the total reactants.

In the production of plasticized products in accordance with this invention, the liquid or solid plasticizer is desirably employed in an amount varying from about 20% to about 80% by weight, basis total weight, and within these limits about 40% to about 60% by weight is preferred. If desired, larger or smaller amounts may be employed in order to effect the desired degree of plasticization.

The plasticized products of the instant invention cannot be produced by first forming the polymerized or cured organic compound containing a urethane or thiourethane group and then incorporating the cured product with the plasticizer. In order to obtain products having satisfactory properties, the organic compound containing the urethane or thiourethane group must be intimately associated with the plasticizer and

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then polymerized or cured to a higher molecular state. In this operation, the organic compound containing the urethane or thiourethane group may be preformed and then added to the plasticizer or it may be formed in situ.

IWhat Is Claim Is:

1. As a new composition of matter, the product obtained by reacting an organic compound containing at least one group selected from the class consisting of urethane and thiourethane groups, with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with said one group of said first-mentioned reactant.

2. As a new composition of matter, the product obtained by reacting an organic compound containing a plurality of groups selected from the class consisting of urethane and thiourethane groups, with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two of said groups of said first-mentioned reactant.

3. As a new composition of matter, the product obtained by reacting an organic polyhydroxy compound with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur and n is an integer having a value of at least 2, and then curing the resulting product by further reaction with an organic compound defined by the above general formula, said second-mentioned reactant being employed in at least one of said reactions in an amount corresponding to at least 30 molar percent excess of the other reactant.

a

4. As a new composition of matter, the product obtained by reacting an organic compound containing a plurality of urethane groups with a compound of the general formula: R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCX, urethane or thiourethane groups, X is selected from the group consisting of oxygen and sulfur and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two urethane groups of said first-mentioned reactant and said reaction being carried out in the presence of a compatible organic liquid which boils at a temperature not less than about 200°C. at atmospheric pressure.

b

5. As a new composition of matter, the cellular product obtained by reacting an organic compound containing a plurality of urethane groups with a compound of the general formula: R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCX, urethane and thio-urethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two urethane groups per mol. of said first-mentioned reactant and said reaction being carried out in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl and substituted hydroxyl groups and precursors of said compounds.

c

6. As a new composition of matter, the cellular product obtained by reacting an organic compound containing a plurality of urethane groups with a compound of the general formula: R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCX, urethane and thio-urethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react at least two urethane groups per mol. of said first-mentioned reactant and said reaction being carried out in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl and substituted hydroxyl groups and precursors of said compounds, and in the presence of a non-reactive organic material having a boiling point of at least 200°C. at atmospheric pressure.

7. The method of preparing a new composition of matter, which comprises reacting an organic compound containing at least one group selected from the class consisting of urethane and thiourethane groups, with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having the value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with said one group of said first-mentioned compound.

8. The method of producing a new composition of matter, which comprises reacting an organic compound containing a plurality of urethane groups with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two urethane groups per mol. of said first-mentioned reactant.

9. The method of producing a new composition of matter, which comprises reacting, in the presence of an organic liquid boiling at a temperature of at least 200°C. at atmospheric pressure, an organic compound containing a plurality of groups selected from the class consisting of urethane and thiourethane groups with a compound of the general formula: $R(ECX)_n$, wherein R is an organic radical free from functional groups other than -ECX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react at least two of said groups per mol. of said first-mentioned reactant.

10. The method of producing cellular products, which comprises reacting, in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl and substituted hydroxyl groups and precursors of said compounds, an organic compound containing a plurality of urethane groups with a compound of the general formula: R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCl, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two urethane groups per mol of said first-mentioned reactant.

11. The method of producing a cellular product, which comprises reacting, in the presence of an organic liquid boiling at a temperature of at least 200°C. at atmospheric pressure, an organic compound containing a plurality of urethane groups with a compound of the general formula: R(N'X)_n, wherein R is an organic radical free from functional groups other than -NCl, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two urethane groups per mol of said first-mentioned reactant and said reaction being carried out in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl and substituted hydroxyl groups and precursors of said compounds.

12. The method of producing a new composition of matter, which comprises reacting an organic polyhydroxy compound with a compound of the general formula: R(NCI)_n, wherein R is an organic radical free from functional groups other than -NCl, urethane and thiourethane groups, and n is an integer having a value of at least 2, and thereby forming an organic compound containing a plurality of urethane groups and then curing the resulting product to a more highly polymerized state by reaction with a compound of the above general formula, said second-mentioned reactant being employed in at least one of said reactions in an amount corresponding to at least 30 molar percent excess of the other reactant.

13. The invention substantially as disclosed and described.

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OATH, POWER OF ATTORNEY, AND PETITION

Being duly sworn, we, James H. Saunders and Herbert L. Neiss, depose and say that we are respectively citizens of the United States, and residents of LaGarde Apts., G-1 and Route 1, Box 166-H, respectively, that we have read the foregoing specification and claims and we verily believe we are the original, first and joint inventors of the invention or discovery in NOVEL RESTRICTED COMPOSITIONS AND METHOD OF PRODUCING SAME, identified as Case A-142 and described and claimed therein; that we do not know and do not believe that this invention was ever known or used before our invention or discovery thereof, or patented or described in any printed publication in any country before our invention or discovery thereof, or more than one year prior to this application, or in public use or on sale in the United States for more than one year prior to this application; that this invention or discovery has not been patented in any country foreign to the United States on an application filed by us or our legal representatives or assigns more than twelve months before this application; and that no application for patent on this invention or discovery has been filed by us or our representatives or assigns in any country foreign to the United States, except as follows:

And we hereby appoint Elmer P. Becker, Registration No. 14540, whose postoffice address is c/o Monsanto Chemical Company, Anniston, Alabama, our attorney or agent with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith.

Wherefore we pray that Letters Patent be granted to us for the invention or discovery described and claimed in the foregoing specification and claims, and hereby subscribe our names to the foregoing specification and claims, oath, power of attorney, and this petition, this 4th day of

August 1953.

Inventor James H. Saunders
 First Name Initial Last Name

Post Office Address LaGarde Apts., G-1

Anniston, Alabama

Inventor Herbert L. Neiss
 First Name Initial Last Name

Post Office Address Route 1, Box 166-H

Anniston, Alabama

Inventor _____
 First Name Initial Last Name

Post Office Address _____

State of Alabama

County of Calhoun

Before me personally appeared James H. Saunders and Herbert L. Neiss,

, to me known to be the persons described in the above application for patent, who signed the foregoing instrument in my presence, and made oath before me to the allegations set forth therein as being under oath, on the day and year aforesaid.

Dorothy J. Waddell

Notary Public

My Commission Expires March 7, 1954

Approved Single Signature Form
 (16.115)

S E A L

NOV-60
REV.
AMERICAN SOCIETY
FOR THE ADVANCEMENT OF SCIENCE
WASHINGTON, D. C.

DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE
WASHINGTON

All communications regarding
this application should address
the Patent Office, Washington,
D. C., or to the Commissioner
of Patents.

PAPER NO. 2

Elmer P. Rucker
c/o Monsanto Chemical Co.
Anniston, Ala.

Please find below a communication from the
EXAMINER in charge of this application.

Elmer P. Rucker
Rucker & Associates
Consultants in Patents

Applicant	J. H. Saunders et al.
Ser. No.	373,036
Filed	Aug. 7, 1953
For NOVEL RESINOUS COM- POSITIONS AND METHOD OF PRODUCING SAME	
	MAILED APR 8 1954 PAT DIV 50

This application has been examined.

References made of record:

Pratt	2,349,756	May 23, 1944	260-77.5A
Schmidt et al.	2,621,166	Dec. 9, 1952	260-77.5A
Seeger (1)	2,625,531	Jan. 13, 1953	260-77.5A
Seeger (2)	2,625,532	Jan. 13, 1953	260-77.5A
Mastin et al.	2,625,535	Jan. 13, 1953	260-77.5A
I.O.P. (1) (French)	869,243	Jan. 27, 1942 (6 pp. spec.)	260-77.5A
I.O.P. (2) (French)	875,643	Sept. 29, 1942 (3 pp. spec.)	260-77.5A
Zellwolle (French)	890,915	Feb. 22, 1944 (3 pp. spec.)	260-77.5A
I.O.P. (3) (French)	897,067	Mar. 12, 1945 (6 pp. spec.)	260-77.5A

De Bell, German Plastics Practice 1946 p. 302
(Copy in Scien. Lib.)

1. The claims are 1-13.
2. Claim 13 is rejected as being obviously informal.
3. Claims 1-12 are rejected as unpatentable over the references cited. Mastin et al., Seeger (1) and (2), and Schmidt et al. cure a polyester-diisocyanate reaction product with more polyisocyanate. Pratt teaches the reaction of di-isocyanates with formaldehyde-urethane resins (page 2, column 2 line 31). I.O.P. as in Example 3 cures a polyurethane with di-isocyanate compounds. Zellwolle shows a similar reaction; note claim 2. Nothing critical is seen in the proportions of claim 3, or the use of a solvent or a catalyst as in certain of the other claims since these do not appear in all the claims; In re Ripper 1949 CD 29; In re Fearn 58 USPQ 403.

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Examiner

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MAY 26 1954

DIVISION 50

MAIL DIVISION
MAY 26 1954
U. S. PATENT OFFICE

IN THE UNITED STATES PATENT OFFICE

IN RE APPLICATION OF :
JAMES H. SAUNDERS ET AL :
SERIAL NO. 373,036 : PAT. DIV. 50
FILED AUG. 7, 1953 :
FOR: NOVEL RESINOUS COM- :
POSITIONS AND METHOD OF PRODUCING
SAME

Commissioner of Patents

Washington 25, D. C.

Sir:

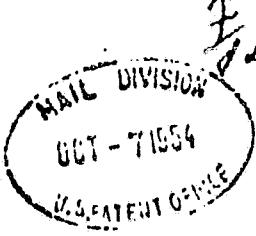
This is to advise you that in the future all correspondence
in connection with the above-entitled application should be sent to the
writer at the following address:

c/o Monsanto Chemical Company
1700 South Second Street
St. Louis, Missouri

Respectfully submitted,

Elmer P. Rucker
Elmer P. Rucker
Attorney of Record

May 21, 1954.



Paper No. 4/a
RECEIVED

OCT 11 1954 D.L.

IN THE UNITED STATES PATENT OFFICE DIVISION 50:

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NUMBER: 373,036

FILED: AUGUST 7, 1953

DIVISION 50

TITLE: NOVEL RESINOUS
COMPOSITIONS AND
METHOD OF PRODUCING
SAME

A M E N D M E N T

The Honorable Commissioner of Patents
Washington 25, D. C.

Sir:

In response to the Office Action dated April 8, 1954,
kindly amend the above-entitled application as follows:

In the specification

Page 14, line 4, insert as title for second column,
the expression --Organic Liquid--.

In the claims

Claim 4, line 4, cancel "or" and insert --and--.

Cancel claims 1-3, 7-8, and 13 without prejudice.

Kindly add the following claims:

Inv. B'

14. As a new composition of matter, the product obtained by reacting an organic compound containing a plurality of groups selected from the class consisting of urethane and thiourethane groups, with a compound of the general formula: R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two of said groups per mol of said first-mentioned reactant and said reaction being carried out in the presence of a non-reactive organic material having a boiling point of at least 200°C. at atmospheric pressure.

*B
A'*

15. As a new composition of matter, the product obtained in accordance with claim 14, wherein the non-reactive organic material is employed in an amount varying from about 20% to 80% by weight, basis total weight.

16. As a new composition of matter, the product obtained in accordance with claim 14, wherein the non-reactive organic material is employed in an amount varying from about 40% to 60% by weight, basis total weight.

Ans. B

17. As a new composition of matter, the cellular product obtained by reacting, an organic compound containing a plurality of groups selected from the class consisting of urethane and thiourethane groups, with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two of said groups per mol of said first-mentioned reactant, and said reaction being carried out in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl and substituted hydroxyl groups and precursors of said compounds.

A 1

18. As a new composition of matter, the cellular product obtained by reacting an organic compound containing a plurality of groups selected from the class consisting of urethane and thiourethane groups, with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two of said groups per mol of said first-mentioned reactant and said reaction being carried out in the presence of a catalyst selected from the group consisting of oxygen bearing compounds yielding in aqueous solution ionizable hydroxyl and substituted hydroxyl groups and precursors of said compounds, and in the presence of a non-reactive organic material having a boiling point of at least 200°C. at atmospheric pressure.

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a'

19. As a new composition of matter, the product obtained in accordance with claim 18, wherein the non-reactive organic material is employed in an amount varying from about 20% to 80% by weight, basis total weight.

20. As a new composition of matter, the product obtained in accordance with claim 18, wherein the non-reactive organic material is employed in an amount varying from about 40% to 60% by weight, basis total weight.

Att B

REMARKS

A correction of an editorial character has been made in the specification.

Claims 1-3, 7-8 and 13 have been cancelled.

Claims 4-6 and 9-12 inclusive were rejected as unpatentable over the references cited and in support of this rejection the Examiner argued as follows:

"Mastin et al., Seeger (1) and (2), and Schmidt et al. cure a polyester-diisocyanate reaction product with more polyisocyanate. Pratt teaches the reaction of diisocyanates with formaldehyde-urethane resins (page 2, column 2 line 31). I.G.P. as in Example 3 cures a polyurethane with diisocyanate compounds. Zellwolle shows a similar reaction; note claim 2. Nothing critical is seen in the proportions of claim 3, or the use of a solvent or a catalyst as in certain of the other claims since these do not appear in all the claims; In re Ripper 1949 CD 29; In re Fehr 58 USPQ 403."

Reconsideration of the above rejection and a favorable action on the claims are courteously solicited in view of the following argument:

The claims now in this application are restricted to the products prepared by reacting an organic compound containing a plurality of urethane or thiourethane groups with a polyisocyanate in the presence of a catalyst and/or a non-reactive organic plasticizer having a boiling point of at least 200°C. and preferably at least 250°C. at atmospheric pressure. These limitations clearly avoid the references of record which at best disclose the use of low boiling solvents as media for reacting polyisocyanates with polyurethanes.

It is respectfully submitted that the claims now in the application define an inventive advance in the art for the following reasons:

Plasticizer

1. The use of a high boiling plasticizer results in the production of flexible cellular and non-cellular products, whereas without such a plasticizer, relatively brittle products of rather limited utility are obtained.

2. The use of high boiling plasticizers, particularly the halogenated ones, results in the formation of products which are quite flame resistant.

3. The use of selected types and amounts of high boiling plasticizers makes possible the production of a series of cellular and non-cellular products of widely varying characteristics. Thus, it is possible to obtain with a single combination of materials a wider range of properties than is possible or practical by varying the polyisocyanate and/or polyol.

4. The use of high boiling plasticizers effects a considerable reduction in the amount of polyisocyanate used to prepare the foaming mixture. This is made possible by the fact that the foaming mixture is more viscous and therefore the tendency of the gas to be liberated is reduced.

5. The high boiling plasticizer stabilizes the polyurethane and the resulting solution can be stored for considerable periods of time at room temperature in tightly closed containers. This solution can then be solidified by heating and in this operation water or other active hydrogen compounds are not required.

Catalyst

1. The use of the catalysts claimed makes possible the production of cellular products by the reaction of polyisocyanates with polyurethanes. No reaction of water with polyisocyanates to form carbon dioxide is required. Moreover, no compounds containing free carboxyl groups are necessary for the foaming reaction.

2. A considerable savings in polyisocyanates is obtained by the use of the catalysts claimed since the former are not partially consumed by reaction with water in the production of carbon dioxide. In other words, all of the polyisocyanate reacts with the polyurethane to yield a polymer of increased molecular weight and therefore less of it is required to yield a cellular product composed of a polymer of a given molecular weight.

3. When employing straight urethanes in the formation of cellular products, a saving is also effected since it is not necessary to utilize the more expensive isocyanates to create the urethane groups.

In view of the foregoing considerations a favorable action on the claims is courteously solicited.

Seven new claims have been incorporated by the present amendment in order to more adequately protect applicants' invention.

Claim 14 is patterned after claim 4, but is broader in scope in that it covers the use of organic compounds containing a plurality of groups selected from the class consisting of urethane and thiourethane groups.

Claims 15 and 16 are based upon claim 14, but are more restricted in scope in that they point out that the non-reactive organic material is employed in an amount varying from about 20% to 80% by weight and from about 40% to about 60% by weight, respectively.

Claim 17 is similar to claim 5, but is broader in scope in that it calls for the use of an organic compound containing a plurality of groups selected from the class consisting of urethane and thiourethane groups.

Claim 18 is similar to 17, but includes the additional limitation to the effect that the reaction is carried out in the presence of non-reactive organic material having a boiling point of at least 200°C. at atmospheric pressure.

Claims 19 and 20 are dependent upon claim 18, but are more restricted in scope in that they specify the amount of the non-reactive organic material employed.

The subject matter of the new claims is not disclosed or suggested by the references of record and therefore, they are believed to be clearly allowable.

This amendment is believed to place the above-entitled application in condition for allowance and an early and favorable action is respectfully requested.

Respectfully submitted,

Elmer P. Rucker

Elmer P. Rucker
Attorney for Applicants

St. Louis, Missouri

October 6, 1954

EPRJa

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FEB 20 1956

IN THE UNITED STATES PATENT OFFICE RECEIVED

Paper No. 5

APPLICATION OF

JAMES H. SAUNDERS ET AL

SERIAL NUMBER: 373,036

FILED: AUGUST 7, 1953

TITLE: NOVEL RESINOUS
COMPOSITIONS AND
METHOD OF PRODUCING
SAME

FEB 23 1956

DIVISION 50

DIVISION 50

POWER OF ATTORNEY

The Honorable Commissioner of Patents

Washington 25, D. C.

Sir:

In the matter of our application for Letters Patent
on NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAME,
filed August 7, 1953, Serial No. 373,036

We hereby appoint F. M. Murdock, Registration No.
15,149 and Donald J. Haefele, Registration No. 15,099, both
of 1700 South Second Street, St. Louis 4, Missouri, or either
of them, as our attorney, with full power of substitution and
revocation, to prosecute this application, to make alterations
and amendments therein, to receive the patent, and to transact
all business in the Patent Office connected therewith. This
appointment is not a revocation of previous powers.

Please address all correspondence to Donald J. Haefele
at the above address.

Signed at New Martinsville, West Virginia, this 13
day of Feb., 1956.

James H. Saunders
James H. Saunders

Herbert L. Neiss
Herbert L. Neiss

from PG-53

DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE
WASHINGTON
MAR

#5

Feb. 27, 1956

F. M. Murdock &
Donald J. Haefele
c/o Monsanto Chemical Co.
1700 S. Second St.
St. Louis, Mo.

Applicant James H. Saunders et al.

Serial No. 373,036

Filed----- Aug. 7, 1953

For ----- novel resinous compositions, etc.

Div. 50

In this case your power of attorney has been accepted.

Very truly yours,

Robert C. Kotter
Commissioner of Patents

-Revoking power of attorney-

to

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ADDRESS SHELF
COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE
WASHINGTON

MAS

Feb. 27, 1956

In re application of
James H. Saunders et al.
Serial No. 373,036
Filed Aug. 7, 1953
novel resinous compositions, etc.
Div. 50

Elmer P. Rucker
c/o Monsanto Chemical Co.
1700 S. Second St.
St. Louis, Mo.

Sir:

On Feb. 20, 1956 the applicants appointed
F. M. Murdock & Donald J. Haefele as their attorneys
in the above application; therefore, further
communications from the Office will be addressed to
Donald J. Haefele, (ex parte Eggan, 172 O.G. 1091).

Very respectfully,

E. L. Carter

Head, Docket Branch

POLICE
B7.
SEARCHED
THE COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

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DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE
WASHINGTON

All communications regarding
this application should give the
Serial number, date of filing,
and name of the applicant.

PAPER NO. 7

Donald J. Haefele
1700 South Second Street
St. Louis, Missouri

Please find below a communication from the
EXAMINER in charge of this application.

Robert C. Kotter
Commissioner of Patents

Applicants:	
James H. Saunders et al.	
Ser. No.	
273,036	
Filed	
August 7, 1953	
For	
NOVEL RESINOUS COM- POSITIONS AND METHOD OF PRODUCING SAME	

MAR 1 ED
OCT 25 1956
PAT 30
DUE 30

Responsive to amendment filed October 7, 1954.

Reference applied:

Simon et al 2,577,281 Dec. 4, 1951 260-2.5A

1. Claims 4 to 6, 9 to 12 and 14 to 20 appear herein.
2. Claims 4 to 6, 9 to 12 and 14 to 20 are rejected
as unpatentable over the references cited in paragraph 3 of the
last Office action. Again, nothing critical is seen in the pro-
portions or the use of a solvent or a catalyst since these do not
appear in all of the claims. In re Ripper 1949 C.D. 29; In re
Pear 56 U.S.P.Q. 403. Furthermore it is well within the purview
of one skilled in the art to know that the use of plasticizers
will prevent the formation of relatively brittle product and also,
that the use of halogenated plasticizers will aid in the formation
of products which are flame retardant.

3. Claims 4 to 6, 9 to 12 and 14 to 20 are rejected as
unpatentable over Mastin et al, Seeger(1) and (2), Pratt, etc. for
the reasons set forth in paragraph 2, supra, in view of Simon et al.
newly cited. Simon et al at columns 11, 12 and 13 disclose that
alkyl esters of aryl phosphoric acids and the trichloralkyl phos-
phates which are used to impart flame resistant properties to the
polyurethane resins also serve as plasticizers. Simon et al may

Serial No. 373,036

-2-

use as high as 25 grams of the polyisocyanate to 30 grams of the polyester (example 9) and varying proportions of the plasticizer (example 3). Contrast this with example 19, for example of the instant application wherein approximately 41 parts of the resin condensate are reacted with 34 parts of the polyisocyanate. To utilize the flame retardant plasticizer as the reaction medium for Mastin et al, Pratt, etc. would not amount to invention.

4. Claims 4 to 6, 9 to 11 and 14 to 20 are rejected as based upon an insufficient disclosure. These claims are drawn to a pre-formed polymer containing a plurality of urethane or thiourethane groups which is then reacted with additional polyisocyanate, whereas the examples only disclose organic polyhydroxy compounds which are reacted with a polyisocyanate. Language in the claims: "said second --- mentioned reactant" (claim 11, lines 8 to 10, for example) is not a sufficient disclosure since Rule 71(b) requires a specific embodiment, viz., an example showing specific proportions of reactants, etc. Claim 12 appears to conform with the examples set forth in the instant application.

5. Claims 4 to 6, 9 to 12 and 14 to 20 are rejected as failing to properly define the alleged invention. The claims are unduly broad in that the proportion of the components are not adequately set forth, and also in the description of the plasticizer. The claims are vague and indefinite in the description of the catalyst. It is obvious that not all such compounds would act as catalysts and yield the applicant his desired results. The claims are too broad, indefinite in the description of the polyisocyanate for example "wherein R is an organic radical". Clarification is required.

6. There is no claim generic to the method claims.

Serial No. 373,036

-3-

The species claims are: 4 to 6, 9 to 12, and 14 to 20. The species are:

- A) Method of Claim 4
- B) Method of Claim 12

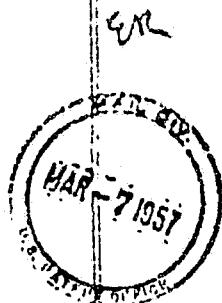
Applicants are required (1) to elect a single disclosed species even though this requirement be traversed and (2) to list all claims readable thereon, including any claims subsequently added.

Section 809.02(a) M.P.E.P.

7. No claim is allowed.

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W.G. Bengel
Examiner



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PAPER NO. 8
RECEIVED

MAR 8 1957

DIVISION 50

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

FILED: August 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

Division 50

The Honorable Commissioner of Patents

Washington 25, D. C.

Sir:

Please recognize CLELL W. UPCHURCH, Registration No. 16,742, of 1700 South Second Street, St. Louis 4, Missouri, as my associate in the matter of the above-entitled application, with full power to prosecute this application, to make alterations and amendments therein, to receive the patent, and to transact all business in the Patent Office connected therewith.

Please address all correspondence to Clell W. Upchurch at the above address.

Signed at St. Louis, Missouri, this 5th day of March, 1957.

Donald J. Neafle
Attorney for Applicants

PAPER NO. 9150
RECEIVED
MAR 14 1957

DIVISION 50

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

FILED: August 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

DIVISION 50

AMENDMENT

The Honorable Commissioner of Patents
Washington 25, D. C.

Sir:

The Official Action dated October 25, 1956, was received
and, in response thereto, please amend the application as follows:

In the claims:

Claims 5 and 6, line 10, before "compounds", insert
-- oxygen bearing --.

Claim 14, line 2, after "reacting", insert -- while
associated with an inert organic plasticizer having a boiling
point of at least about 200°C. --; line 11, after "reactant",
insert -- a period -- and cancel the remainder of the claim.

Claim 17, line 2, after "reacting", insert -- while
associated with a catalyst selected from the group consisting of
oxygen bearing compounds yielding in aqueous solution ionizable
hydroxyl and substituted hydroxyl groups and precursors of said
compounds --; line 11, after "reactant", insert -- a period -- and
cancel the remainder of the claim.

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MAR 14 1957

DIVISION 50

Claim 18, line 13, before "compounds", insert -- oxygen bearing ---.

Cancel claims 9 through 12.

Insert the following claims:

-- 21. In the manufacture of polyurethane products by a process comprising reacting an organic compound having reactive hydrogen atoms with a compound having NCX groups, wherein X is selected from the class consisting of O and S atoms, to form an adduct having groups selected from the class consisting of urethane and thiourethane groups, and reacting NCX groups with the active hydrogen atoms of the resulting urethane and thiourethane groups in said adduct, the improvement which comprises effecting the last said reaction while the adduct is associated with an inert organic plasticizer.

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MAR 14 1957

DIVISION 50

22. In the manufacture of polyurethane products by a process comprising reacting an organic compound having reactive hydrogen atoms with a compound having NCX groups, wherein X is selected from the class consisting of O and S atoms, to form an adduct having groups selected from the class consisting of urethane and thiourethane groups, and reacting NCX groups with the active hydrogen atoms of the resulting urethane and thiourethane groups in said adduct, the improved method of making a flexible cellular product which comprises adding as a catalyst an oxygen bearing compound which yields in aqueous solution a group selected from the class consisting of ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds to a solution of said adduct comprising an organic plasticizer having a boiling point of at least about 200°C. thereby bringing about the last said reaction.

23. In the manufacture of polyurethane products by a process comprising reacting an organic compound having reactive hydrogen atoms with a compound having NCX groups, wherein X is selected from the class consisting of O and S atoms, to form an adduct having groups selected from the class consisting of urethane and thiourethane groups, and reacting NCX groups with the active hydrogen atoms of the resulting urethane and thiourethane groups in said adduct, the improvement which comprises effecting the last said reaction by heating said adduct while associated with an inert organic plasticizer having a boiling point of at least about 200°C.

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MAR 14 1957

DIVISION 50

24. In the manufacture of polyurethane products by a process comprising reacting an organic compound having reactive hydrogen atoms with a compound having NCX groups, wherein X is selected from the class consisting of O and S atoms, to form an adduct having groups selected from the class consisting of urethane and thiourethane groups, and reacting NCX groups with the active hydrogen atoms of the resulting urethane and thiourethane groups in said adduct, the improvement which comprises effecting the last said reaction while the adduct is dissolved in an inert organic plasticizer having a boiling point of at least about 200°C.

25. In the manufacture of polyurethane products by a process comprising reacting an organic compound having reactive hydrogen atoms with a compound having NCX groups, wherein X is selected from the class consisting of O and S atoms, to form an adduct having groups selected from the class consisting of urethane and thiourethane groups, and reacting NCX groups with the active hydrogen atoms of the resulting urethane and thiourethane groups in said adduct, the improvement which comprises effecting the last said reaction while the adduct is associated with a catalyst which is an oxygen bearing compound selected from the group consisting of compounds which yield in aqueous solution ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds.

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PAPER NO.
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MAR 14 1957

DIVISION 50

26. In the manufacture of polyurethane products by a process comprising reacting an organic compound having reactive hydrogen atoms with a compound having NCX groups, wherein X is selected from the class consisting of O and S atoms, to form an adduct having groups selected from the class consisting of urethane and thiourethane groups, and reacting NCX groups with the active hydrogen atoms of the resulting urethane and thiourethane groups in said adduct, the improvement which comprises effecting the last said reaction while the adduct is associated with an inert organic plasticizer having a boiling point of at least about 200°C. and a catalyst which is an oxygen bearing compound selected from the group consisting of compounds which yield in aqueous solution ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds.

27. The method which comprises reacting a compound having as its sole reactive groups NCX groups and the groups selected from the class consisting of urethane and thiourethane groups wherein X is selected from the group of atoms consisting of O and S atoms, with a compound having NCX groups while associated with an inert organic plasticizer having a boiling point of at least about 200°C.

28. The method which comprises reacting a compound having as its sole reactive groups NO_X groups and the groups selected from the class consisting of urethane and thiourethane, wherein X is selected from the group of atoms consisting of O and S atoms, with a compound having NCX groups while associated with a catalyst which is a compound selected from the class consisting of oxygen bearing compounds which yield in aqueous solution ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds.

29. The method which comprises reacting a polyhydroxy compound having as its sole reactive groups NCX groups and the groups selected from the class consisting of urethane and thiourethane groups wherein X is selected from the group of atoms consisting of O and S atoms, with a compound having NGX groups while associated with an inert organic plasticizer having a boiling point of at least about 200°C. --

R E M A R K S

Reconsideration of the application in view of the foregoing amendments and the following explanation is respectfully requested.

It is submitted that no possible combination of the references will produce applicants' novel process. The patent to Pratt discloses the reaction of a phenol formaldehyde resin with

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MAR 14 1957

DIVISION 50

a polyisocyanate to form a polyurethane. There is no teaching in the patent of the reaction of a compound having a urethane group with an NCX group while associated with either a plasticizer or the novel catalyst recited by applicants' claims. It is true that Pratt discloses a urethane in Column 2 of page 2, but he does not disclose the organic plasticizer or the catalyst.

The patents to Seeger, 2,625,531 and 2,625,532, disclose processes for reacting a polyester with a diisocyanate but this reaction is not brought about while associated with an organic plasticizer or while associated with the novel catalyst of applicants' claims.

Schmidt et al., 2,621,166, disclose a process which involves reacting a polyester with a diisocyanate, cross-linking with an amino hydroxy compound or amine and then further reacting with a diisocyanate. Schmidt et al. did not bring about their reactions in the presence of an organic plasticizer or applicants' novel catalyst.

The Simon et al. patent, 2,577,281, relates to the preparation of a flame retardant cellular plastic material by incorporating an alkyl ester of an aryl phosphoric acid in the plastic. Simon et al. did not contemplate and do not disclose applicants' method of making a flexible polyurethane plastic by bringing about the reaction between the urethane group and the NCX group while associated with a plasticizer. Neither did these inventors contemplate the reaction in the presence of a novel catalyst recited by applicants' claims.

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Mastin et al., in 2,625,535, disclose a process for reacting a diisocyanate-modified polyester with a particular diisocyanate, but applicants' process of reacting the compounds together while in the presence of a plasticizer or novel catalyst is not disclosed.

As applicants have pointed out in the last paragraph of their specification, the reaction between the compound having the urethane or thiourethane group with the isocyanate or thioisocyanate group must be brought about in the presence of the plasticizer in order to obtain a product having the improved flexibility. If the reaction is brought about in the absence of a plasticizer and the plasticizer is then added to the product as disclosed in the various patents discussed in paragraph 3 of the Office Action, the result is not obtained. Applicants, therefore, are not merely adding a plasticizer to a polyurethane product to produce flexibility. They found that the reaction must be brought about while the reactants are associated with the plasticizer and claim such a process. The term "organic plasticizer" has been used to describe the organic liquids and solvents making up the class of compounds described in the specification. Several illustrative examples of such compounds are listed in the last paragraph, page 6.

Applicants' cellular product is prepared in accordance with their invention by bringing about the reaction between the compound having the urethane group or thiourethane group with the isocyanate or thioisocyanate group while associated with a

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catalyst which yields ionizable hydroxyl groups in aqueous solution. This preparation is novel and produces a cellular plastic having unexpected advantageous characteristics. A flexible cellular plastic may be prepared by bringing about the reaction while the compound having the urethane group and the isocyanate are associated with both the catalyst and the plasticizer. Such a process is not contemplated by the references, so it is felt that the claims are allowable.

It is believed evident from the foregoing that applicants do not rely solely upon the proportions recited by some of the claims to contribute patentability to their process, so the In re Ripper and In re Fear doctrines are not applicable. It may be that those skilled in the art know that a plasticizer should be used to avoid a brittle product, but, as pointed out above, those in the prior art did not know and do not teach that the plasticizer must be present while the reaction is brought about. The product of claims 4 through 6 and 14 through 20 or the process of the other claims is not produced by the prior art relied upon.

The various rejections of paragraph 3 are felt to be improper because the patents do not disclose that the reaction must be brought about in the presence of a plasticizer.

With respect to the rejection in paragraph 4, the Examiner's attention is directed to the last sentence on page 1 of the specification where applicants disclose that sufficient NCX groups should be used to react with at least two urethane groups. Of the rejected claims, claims 4 through 6 and 9 through 12 have

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been canceled. The newly added claims do not contain this limitation, but it is felt that it can be properly included in claims 14 through 20 in view of the foregoing disclosure.

It is submitted that the claims are commensurate with applicants' disclosure. Applicants have taught broadly their novel reaction in the presence of the plasticizer and obviously the proportions of components are not critical. The result is brought about because the plasticizer and catalyst are present. It is felt, therefore, that the suggested numerical limitations would unduly limit the claims and are unnecessary. Anyone reading the specification would understand the type of catalyst applicants claim and that any organic isocyanate suitable for making polyurethanes may be used. Insofar as applicants know, any oxygen bearing catalyst which ionizes to form hydroxyl groups in aqueous solution will be suitable for their purpose and they have disclosed that such catalyst may be used. It is therefore felt that the rejection in paragraph 5 should be withdrawn.

The newly added claims 21 through 26 have been rewritten in the *In re Jepson* form to point up that applicants' invention involves bringing about the reaction while the adduct is associated with an inert organic plasticizer and applicants' novel catalyst. It is believed that the invention is clearly defined by these claims. Claim 22 differs from claim 21 by specifying the minimum boiling point of the plasticizer and by also requiring the use of the catalyst to produce a cellular product. Claim 23 differs from claim 21 by reciting the boiling point of the plasticizer. Claim 24 states that the compounds are

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dissolved in the organic plasticizer. Claim 25 is directed to the method using the novel catalyst for making a cellular product while claim 26 recites a process in which both an organic plasticizer and the catalyst are used. It differs from claim 22 by not reciting that a flexible cellular product is produced. Claims 27 and 28 are not in the In re Jepson type but briefly recite the specific step of reacting the organic compound having the urethane groups with the NCX groups while associated with the plasticizer and catalyst, respectively. Claim 29 is similar to claim 27 but recites "polyhydroxy compound." These claims differ from the other claims in their form and it is believed that they, along with the other claims will be found allowable.

The requirement of an election of species is not understood since claim 4 is not a method claim. However, it appears that the Examiner is referring to the fact that no plasticizer or catalyst is included in claim 12. Claim 12 has been canceled and catalyst or plasticizer appears in each of the other claims. Applicants therefore elect the species of claim 4 and are of the opinion that each of them reads on the same species.

It is believed that the foregoing is a complete response to the Official Action and that each of the claims remaining in the application will be found allowable. Favorable reconsideration with allowance of the claims is therefore earnestly solicited.

Respectfully submitted,

JAMES H. SAUNDERS
HERRBERT L. HEISS

By Clelie W. Upchurch
Clelie W. Upchurch
Attorney for Applicants

St. Louis, Missouri
March 8, 1957
CWU:gg

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Rev.
AMERICAN COUNSEL
THE CHIEF COUNSELOR OF PATENTS
WASHINGTON D. C.

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U. S. DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE
WASHINGTON

All communications respecting
this application should give the
serial number, date of filing,
and name of the applicant.

PAPER NO. 10

Clellie W. Upchurch
1700 South Second Street
St. Louis, Missouri

Please find below a communication from the
EXAMINER in charge of this application.

Robert Chotter
Commissioner of Patents.

Applicant:	James H. Saunders et al.	
Ser. No.	373,036	
Filed	Aug. 7, 1953	
For NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAME		MAILED JUL 31 1957 PAT 50 D.W. 1957

Responsive to amendment filed March 12, 1957.

References made of record:

Rinke et al 2,511,544 June 13, 1950 260-77.5A
Simon et al (2) 2,772,245 Nov. 27, 1956 260-2.5A
(Filed Apr. 26, 1952)

1. Claims 4 to 6 and 14 to 29 appear herein.
2. Claims 4, 14 to 16, 21, 23, 24, 27 and 29 are rejected as unpatentable over Rinke et al. This reference discloses the reaction of a compound containing active hydrogens with an organic polyisocyanate in the presence of an inert organic liquid having a boiling point of at least about 200°C. See column 1, line 54 and example 23 of Rinke et al, for example. No patentable distinction is seen in applicants' claimed order of reaction since they disclose that the adducts can be formed in situ in the organic liquid which is taught by Rinke et al. Nothing critical is seen in applicants' claimed percentage of organic liquid. See page 20, lines 23 and 24 of the specification.

3. Claims 5, 6, 17 to 20, 22, 25, 26 and 28 are rejected as unpatentable over Simon et al (2) alone or taken with Rinke et al as set forth in paragraph 2 supra. Simon et al. (2) disclose applicants' claimed type of catalyst which is used in the production of cellular resins from active hydrogen

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containing compounds and organic polyisocyanates. See column 3, line 60 to column 4, line 75 of Simon et al, for example. Nothing critical is seen in applicants' claimed order of reaction nor in the use of the organic liquid. Rinke et al disclose the preparation of applicants' adducts in an organic liquid as the reaction medium. To try the catalysts of Simon et al (2) in the process of Rinke et al so as to produce a cellular resin would not involve invention.

4. Claims 4 to 6 and 14 to 29 are rejected as based upon an insufficient disclosure as set forth in paragraph 4 of the last Office action. The statement on page 1, last sentence, is nothing more than an invitation to the public to experiment and determine what proportions are operative. The method set forth in claims 21 to 29 is ambiguous and can therefore be interpreted to mean that additional diisocyanate is added. To reply that it would be within the purview of one skilled in the art to determine the proportions would be of no moment since Rule 71(b) has no reference to one skilled in the art.

5. Claims 4 to 6 and 14 to 29 are rejected as being unduly multiplied. No patentable distinction is seen in the Jepson type claims (21 to 26) over the other claims in the case. Reduction to a reasonable number of claims, say 12 claims, is in order.

6. Claims 4 to 6 and 14 to 29 are further rejected as failing to properly define the alleged invention. All claims 4 to 6 and 14 to 29 are unduly broad in the phrases, "an organic compound containing a plurality of urethane groups" and "an organic compound containing a plurality of groups selected from

the class consisting of urethane and thiourethane groups", respectively. The above phrases encompass polyvinylpyrrolidone or the reaction product of chlorocarbonic acid ester with hydrazine which have not been disclosed as operative. B) Claims 4 to 6 and 14 to 20 are indefinite in "R(NCS)_n", wherein R is an organic---of at least 2" in that negative limitations should not be used in the claims. C) Claims 21 to 26 are too broad in the phrase "an organic compound having reactive hydrogen atoms" since this reads on epoxy resins which contain active hydrogen, polyvinyl alcohol, etc. which have not been disclosed. D) Claims 21 to 29 are too broad in the phrase "a compound having NCM groups---O and S atoms" and claims 27 to 29 are too broad in "with a compound having NCX groups" since it reads on calcium diisocyanate, silicone tetraisocyanate, etc. which have not been disclosed. E) The phrases "a compatible organic liquid---at atmospheric pressure" (claims 4 and 6), "inert organic---about 200°C" (claim 14), "non-reactive organic---pressure" (claim 18), inert organic plasticizer (claim 21) and "an organic---about 200°C" (claims 22 to 24, 26 and 29) which are used to define the organic liquid reaction medium are unduly broad and indefinite. It is not seen wherein all the compounds encompassed by the above phrases would be operative. Furthermore, some of the claims read on plasticizers which have low boiling points, e.g. 75°C or less, which have not been disclosed as operative for applicants' purposes. See page 6, line 12. F) The phrase "a catalyst selected from the group consisting of oxygen---hydroxyl groups and precursors of said compounds" which appears in claims 5, 6, 17 to 20, 22, 25, 26 and 28 is too broad. The use of such broad language in the claims is not warranted in view of applicants' limited disclosure. As to rejection E and F supra: By the use of such broad language

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in the claims applicants are merely extending an invitation to the public to experiment and determine just what other compounds would be operative in applicants' process. In this respect see *In re Soll* 1938 C. D. 723. G) Claims 25, 26 and 28 appear to be incomplete in that they call for the presence of a catalyst which would therefore yield a cellular resin. Therefore, some language denoting that a cellular resin is obtained should be inserted in the claims. H) All the claims are too broad in that the ratio of the polyisocyanate to the adduct is not set forth. The claims as they now stand read on such amounts which would yield inoperative results. See page 5, lines 6 to 15.

7. No claim is allowed.

J. H. Easton

DCCB:jat:bg

Examiner

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JAN 17 1953

IN THE UNITED STATES PATENT OFFICE DIVISION 50

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

DIVISION 50

FILED: August 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

The Honorable Commissioner of Patents
Washington 25, D. C.

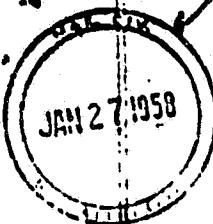
Sir:

Please address all future correspondence in the above
identified application to:

Clelle W. Upchurch
1815 Washington Rd.
Pittsburgh 34, Pennsylvania

Respectfully,

Clelle W. Upchurch
Clelle W. Upchurch



PAPER NO 12/1
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IN THE UNITED STATES PATENT OFFICE JAN 30 1958

DIVISION 50

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

FILED: August 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

DIVISION 50

The Honorable Commissioner of Patents

Washington 25, D. C.

Sir:

AMENDMENT

The Office Action dated July 31, 1957, was received and,
in response thereto, the application is amended as follows:

Please cancel all the claims and rewrite them as
follows:

--(30. As a new composition of matter, the product obtained by mixing a compound having the formula R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer of at least 2, with an organic compound having hydrogen atoms reactive with said -NCX groups, the ratio of R(NCX)_n to organic compound having reactive hydrogens being greater than 1:1, and thereafter maintaining the resulting adduct under substantially anhydrous conditions until polymerization with the formation of a product of greater molecular weight.

1. P (31) As a new composition of matter, the product obtained by mixing a compound having the formula $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer of at least 2, with an organic compound having hydrogen atoms reactive with said -NCX groups, the ratio of $R(NCX)_n$ to organic compound having reactive hydrogens being greater than 1:1, and thereafter heating the resulting adduct under substantially anhydrous conditions and at a temperature of at least about 60°C . until polymerization with the formation of a product of greater molecular weight.

1. P (32) As a new composition of matter, the product obtained by mixing a compound having the formula $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer of at least 2, with an organic compound having hydrogen atoms reactive with said -NCX groups, the ratio of $R(NCX)_n$ to organic compound having reactive hydrogens being greater than 1:1, and thereafter heating the resulting adduct under substantially anhydrous conditions and at a temperature of from about 100°C . to about 125°C . until polymerization with the formation of a product of greater molecular weight.

~~33. As a new composition of matter, the product obtained by mixing a compound having the formula R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer of at least 2, with an organic compound having hydrogen atoms reactive with said -NCX groups, the ratio of R(NCX)_n to organic compound having reactive hydrogens being greater than 1:1, and an inert compatible organic plasticizer having a boiling point of at least about 200°C.~~

~~C 1~~
~~34. As a new composition of matter, the product obtained by mixing a compound having the formula R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer of at least 2, with an organic compound having hydrogen atoms reactive with said -NCX groups, the ratio of R(NCX)_n to organic compound having reactive hydrogens being greater than 1:1, and thereafter heating at a temperature of at least about 60°C. a mixture of the resulting adduct and an inert compatible organic liquid having a boiling point of at least about 200°C.~~

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~~35. The reaction product of a triol prepared by condensation of an alkylene oxide and an organic trihydroxy compound and an excess of a compound having the formula R(NCX)_n over that required to react with all of the hydroxyl groups of the triol; R in said formula being an organic radical, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.~~

37. A cured polyurethane prepared by a process comprising mixing a compound having the formula $R(NCX)_n$ with an organic compound having hydrogens reactive with an -NCX group, the ratio of said reactants in the resulting mixture being more than 1 mol of $R(NCX)_n$ per mol of compound having reactive hydrogens, and curing the resulting product while in admixture with a compound having the formula $R(NCX)_n$; R being an organic radical, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

38. The product prepared by reacting castor oil with a compound having the formula $R(NCX)_n$ to form an adduct having terminal -NCX groups and thereafter heating the adduct under substantially anhydrous conditions to a temperature of at least about 60°C. to effect polymerization; R in said formula being an organic radical, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

39. The product prepared by reacting castor oil with a compound having the formula $R(NCX)_n$ to form an adduct having terminal -NCX groups and thereafter heating the adduct while in admixture with an inert compatible organic liquid having a boiling point of at least about 200°C. to effect polymerization; R in said formula being an organic radical, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

40. A cellular polyurethane plastic prepared by reacting a compound having the formula $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer of at least 2, with an organic compound having hydrogen atoms reactive with said -NCX groups while in admixture with a catalyst which is an oxygen bearing compound yielding in aqueous solution a group selected from the class consisting of ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds.

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41. A cellular polyurethane plastic prepared by reacting under substantially anhydrous conditions a compound having the formula $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer of at least 2, with an organic compound having hydrogen atoms reactive with said -NCX groups while in admixture with a catalyst which is an oxygen bearing compound yielding in aqueous solution a group selected from the class consisting of ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds.

42. A cellular polyurethane plastic prepared by reacting a compound having the formula $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer of at least 2, with a triol prepared by condensation of an alkylene oxide and an organic trihydroxy compound while in admixture with a catalyst which is an oxygen bearing compound yielding in aqueous solution a group selected from the class consisting of ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds.

43. A cellular polyurethane plastic prepared by reacting a compound having the formula $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer of at least 2, with an organic compound having hydrogen atoms reactive with said -NCX groups while in admixture with a compatible organic liquid plasticizer having a boiling point of at least about 200°C. and a catalyst which is an oxygen bearing compound yielding in aqueous solution a group selected from the class consisting of ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds.

44. A plasticized cellular polyurethane prepared by a process comprising mixing castor oil with an excess of a compound having the formula $R(NCX)_n$ over that required to react with all the hydroxyl groups of the castor oil and reacting the said compounds together and effecting foaming while in admixture with an organic liquid plasticizer having a boiling point of at least about $200^{\circ}\text{C}.$, thereby incorporating said plasticizer in the resulting cellular polyurethane.

45. In the preparation of polyurethanes by a process comprising reacting (a) compound having the formula $R(NCX)_n$ with an organic compound having hydrogen atoms reactive with $-NCX$, R in the said formula being an organic radical, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2, the improvement which comprises effecting the said reaction (in the presence of a catalyst containing) a lower alkyl-N-morpholine.

46. The process of Claim 45 wherein said lower alkyl-N-morpholine is methyl-N-morpholine.

47. The process of Claim 45 wherein said lower alkyl-N-morpholine is ethyl morpholine.

48. A method for making polymers which comprises mixing a compound having the formula $R(NCX)_n$ with an organic compound having hydrogen atoms reactive with said -NCX groups in a ratio of $R(NCX)_n$ to organic compound having reactive hydrogen atoms of more than 1:1, respectively, and thereafter maintaining the resulting adduct under substantially anhydrous conditions until polymerization with the formation of a product of greater molecular weight; R in the foregoing formula being an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

49. A method for making polymers which comprises mixing a compound having the formula $R(NCX)_n$ with an organic compound having hydrogen atoms reactive with said -NCX groups in a ratio of $R(NCX)_n$ to organic compound having reactive hydrogen atoms of more than 1:1, respectively, and thereafter heating the resulting adduct under substantially anhydrous conditions and at a temperature of at least about 60°C. until polymerization with the formation of a product of greater molecular weight; R in the foregoing formula being an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

50. A method for making polymers which comprises mixing a compound having the formula $R(NCX)_n$ with an organic compound having hydrogen atoms reactive with said -NCX groups in a ratio of $R(NCX)_n$ to organic compound having reactive hydrogen atoms of more than 1:1, respectively, and thereafter heating the resulting adduct under substantially anhydrous conditions and at a temperature of from about 100°C. to about 125°C. until polymerization with the formation of a product of greater molecular weight; R in the foregoing formula being an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

51. A method for making polymers which comprises mixing a compound having the formula $R(NCX)_n$ with an organic compound having hydrogen atoms reactive with said -NCX groups in a ratio of $R(NCX)_n$ to organic compound having reactive hydrogen atoms of more than 1:1, respectively, and an inert compatible organic liquid having a boiling point of at least about 200°C. and maintaining the resulting mixture under substantially anhydrous conditions until polymerization with the formation of a product of greater molecular weight; R in the foregoing formula being an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

52. A method for making polymers which comprises mixing a compound having the formula $R(NCX)_n$ with an organic compound having hydrogen atoms reactive with said $-NCX$ groups in a ratio of $R(NCX)_n$ to organic compound having reactive hydrogen atoms of more than 1:1, respectively, and thereafter heating at a temperature of at least about $60^{\circ}C$. a mixture of the resulting adduct and an inert, compatible organic liquid having a boiling point of at least about $200^{\circ}C$. until polymerization with the formation of greater molecular weight; R in the foregoing formula being an organic radical free from functional groups other than $-NCX$, urethane and thiourethane groups, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

53. A method for making a plastic which comprises reacting the condensation product of an alkylene oxide and an organic trihydroxy compound with a compound having the formula $R(NCX)_n$ present in the reaction mixture in an amount in excess of that required to react with said condensation product; R in said formula being an organic radical, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

54. A method for making a plastic which comprises reacting a triol prepared by condensation of an alkylene oxide and an organic trihydroxy compound with a compound having the formula $R(NCX)_n$ present in the reaction mixture in an excess over that required to react with all of the hydroxyl groups of the triol, and thereafter curing the resulting adduct by a process which comprises heating the adduct to a temperature of at least 60°C. while in admixture with an inert compatible organic liquid boiling at a temperature of at least about 200°C.; R in said formula being an organic radical, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

55. A method for making a polyurethane which comprises reacting a compound having the formula $R(NCX)_n$ with an organic compound having hydrogen atoms reactive with an -NCX group, the ratio of the reactants in the reaction mixture being more than 1 mol of $R(NCX)_n$ per mol of the other said reactant, and curing the resulting product while in admixture with a compound having the formula $R(NCX)_n$; R in said formula being an organic radical, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

56. A method for making a polyurethane which comprises reacting castor oil with a compound having the formula $R(NCX)_n$ to form an adduct having terminal -NCX groups and thereafter heating the adduct under substantially anhydrous conditions to a temperature of at least about 60°C. to effect polymerization; R in said formula being an organic radical, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

57. A method for making a polyurethane which comprises reacting castor oil with a compound having the formula $R(NCX)_n$ to form an adduct having terminal -NCX groups and thereafter heating the adduct while in admixture with a compatible liquid having a boiling point of at least about 200°C. to effect polymerization; R in said formula being an organic radical, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

58. A method for making a cellular polyurethane which comprises reacting a compound having the formula $R(NCX)_n$ with an organic compound having hydrogen atoms reactive with said -NCX groups while in admixture with a catalyst which is an oxygen bearing compound yielding in aqueous solution a group selected from the class consisting of ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds; R in said formula being an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

59. A method for making a cellular polyurethane which comprises reacting under substantially anhydrous conditions a compound having the formula $R(NCX)_n$ with an organic compound having hydrogen atoms reactive with said $-NCX$ groups while in admixture with a catalyst which is an oxygen bearing compound yielding in aqueous solution a group selected from the class consisting of ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds; R in said formula being an organic radical free from functional groups other than $-NCX$, urethane and thiourethane groups, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

60. A method for making a cellular polyurethane which comprises reacting a compound having the formula $R(NCX)_n$ with a triol prepared by condensation of an alkylene oxide and an organic trihydroxy compound while in admixture with a catalyst which is an oxygen bearing compound yielding in aqueous solution a group selected from the class consisting of ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds; R in said formula being an organic radical free from functional groups other than $-NCX$, urethane and thiourethane groups, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

61. A method for making a cellular polyurethane which comprises reacting a compound having the formula $R(NCX)_n$ with an organic compound having hydrogen atoms reactive with said -NCX groups while in admixture with a compatible organic liquid plasticizer having a boiling point of at least about 200°C. and a catalyst which is an oxygen bearing compound yielding in aqueous solution a group selected from the class consisting of ionizable hydroxyl groups, substituted hydroxyl groups and precursors of such compounds; R in said formula being an organic radical free from functional groups other than -NCX, urethane and thiourethane groups, X being selected from the group consisting of oxygen and sulfur and n being an integer of at least 2.

62. The process of Claim 58 wherein said catalyst is an alkali metal hydroxide.

63. The process of Claim 58 wherein the catalyst is an alkali metal oxide.

64. The process of Claim 58 wherein the catalyst is calcium hydroxide.

65. The process of Claim 58 wherein the catalyst is an oxide of a metal of Group II of the Periodic Table.

66. The process of Claim 58 wherein the catalyst is benzyl trimethyl ammonium hydroxide. --

REMARKS

Reconsideration of the application in view of the foregoing amendment and the following explanation is respectfully requested:

All of the claims have been canceled and replaced with a new set of claims which more fully claims the invention. Applicants were not unmindful of the Examiner's statement in paragraph 5 of the Office Action in presenting the new set of claims. They have made an attempt to reduce the number of claims but have found that the invention cannot be fully claimed with a smaller number of claims than those presented herewith. As will become apparent hereinafter, no two claims overlap each other.

None of the claims presented herewith can be properly rejected on Rinke et al. Rinke et al. prepare a product in the presence of an organic liquid. The product of Rinke et al. is prepared from a monomeric hydroxy compound and an organic polyisocyanate. As is clearly brought out in each example, the Rinke et al. product precipitates from the solvent and the solvent is removed. Applicants, on the other hand, prepare a product which contains a plasticizer. Applicants do not remove their plasticizer from the product. It is absorbed or otherwise becomes dispersed in the product and remains there after solidification or gelling.

It is believed that the Examiner has overlooked that applicants' process for making the cellular polyurethane does not require the presence of water to produce the pore structure. Bubbles are formed in the reaction mixture when the isocyanate is reacted with the organic compound having reactive hydrogens in the presence of the novel catalysts recited in Claims 40 through 44 and 58 through 66 whether water is present or not. Simon et al. prepare a foam by the well-known process of mixing water with the

isocyanate and organic compound having reactive hydrogens. The water reacts with NCO groups to form carbon dioxide which becomes entrapped in the reaction mixture and is the sole source of porosity in the product. No completely satisfactory explanation is available of the reaction which brings about the bubbling in applicants' reaction mixture. Water is not required but it does not necessarily have to be excluded from the reaction mixture. It is possible to supplement the formation of bubbles brought about by the catalyst with bubbles formed by reaction of water with an -NCO group. This is brought out in the specification where it is stated that the reaction may be conducted in the presence or absence of water. However, it is preferred, at least in some instances, to operate under the substantially anhydrous conditions of Claim 59. It is believed obvious from the foregoing explanation that no possible combination of Simon et al. with Rinke et al. will produce the novel process for making a cellular polyurethane without the requirement that water be included in the reaction mixture.

The claims no longer include the phrase objected to in Paragraph 4. The claims now require an excess of the isocyanate over that required to react with the reactive hydrogens of the other compound.

The phrases objected to in Paragraph 6A do not appear in the new claims.

It is submitted that the definition of the formula used in the claims is proper and consistent with past procedure. It is not understood how the claims can be rejected on the basis that

the definition of the formula uses negative limitations. The terminology, "free from functional groups", appears in many patents and has met with the approval of the Board of Appeals and the Court of Customs and Patent Appeals. The limitation on the numerical value of n is not negative because it states in positive language that it must be at least 2.

The only requirement of the organic compound having reactive hydrogens is that the hydrogen atoms be reactive with -NCX groups. This is clearly brought out in the specification and the claims now employ such language. The claims no longer read on the diisocyanates mentioned in Paragraph 6D. They now require that R be an organic radical.

As is apparent from the specification, and particularly page 6, and the working examples, any organic compound which will plasticize the product may be used. The plasticizer may be either a solid or liquid. It must be inert and must be compatible with the product. The claims require that it have these properties. They also require that the boiling point be at least about 200°C. which further distinguishes the product and process from Rinke et al. The Examiner is reminded that applicants have provided a basic invention in which the plasticizer is incorporated in the product by having it present when chemical reaction occurs. The invention lies in finding that the plasticizer must be placed in the product at this time and not in finding a particular plasticizer which will work. As pointed out in the specification, the product will not have the desirable physical characteristics if the plasticizer is incorporated therein after chemical reaction.

It is therefore submitted that applicants are entitled to claims which broadly cover the process of incorporating the plasticizer in the mixture before complete chemical reaction.

With respect to paragraph 6F, it is pointed out that no one has heretofore prepared polyurethane foams by a process where bubbling in the reaction mixture is achieved through selection of the catalyst. Applicants have disclosed broadly that any compound having hydroxyl groups, substituted hydroxyl groups or precursors of such compounds will produce the desired result. In the absence of some disclosure which requires that the claims be more limited than they are at the present time, it is submitted that they should be allowed. The disclosure clearly supports the broad claims. The Examiner is referred to the last paragraph beginning on page 19 and continuing on page 20.

The claims now specify the ratio of polyisocyanate to organic compound having reactive hydrogens.

As indicated hereinbefore, the present set of claims is required to properly cover the invention. Claims 30, 31 and 32 are product claims covering the product obtained by polymerization of the adduct. None of the references discloses this process because all of the references use a cross-linker. Please note that applicants do not use a cross-linker. Applicants' chain extension or cross-linking is believed to be achieved through reaction of the -NCX groups of the adduct or any monomeric isocyanate present with the reactive hydrogen atoms of the urethane or thiourethane linkages. Chain extension may also occur through polymerization of the -NCX groups with the formation of a

heterocyclic ring. Always heretofore, a chain extender, such as water, a diamine, a glycol or the like, has been used for this purpose. Claims 48 through 50 cover the process for making this product.

Claims 33 and 34 are directed to a product prepared by effecting chemical reaction and polymerization while the adduct is in admixture with the plasticizer. Claims 51 and 52 cover the process for making this product.

Claims 35 and 36 are directed to a polyurethane prepared from the condensation product of an alkylene oxide and an organic trihydroxy compound and an excess of an isocyanate or thioisocyanate. This product is disclosed as a preferred embodiment in several of the working examples and elsewhere in the specification. Claims 53 and 54 cover the process of making the product.

Claim 37 is directed to the preparation of a cured polyurethane wherein some monomeric $R(NCX)_n$ is present during the chain extension.

Claims 38 and 39 are directed to a product prepared from castor oil and polymerization of the adduct to bring about the chain extension. These claims clearly distinguish from any prior disclosure because no one has heretofore prepared a castor oil-isocyanate adduct and then effected chain extension without a chain extender. Claims 56 and 57 are directed to the process for preparing this novel product.

Claims 40 through 44 are directed to a cellular polyurethane prepared with the novel catalyst disclosed in the

specification. Claim 41 is specific to a process wherein substantially anhydrous conditions are employed. Claim 42 is specific to the preparation of the adduct from the condensation product of an alkylene oxide and an organic trihydroxy compound. Claim 43 is directed to the product containing the plasticizer provided by this invention. Claim 44 is specific to a cellular polyurethane prepared from castor oil and the plasticizer. Claims 58 through 66 are directed to the process for making the cellular polyurethane with the novel catalyst which effects foaming.

Claims 45 through 47 are directed to the preparation of polyurethanes with the N-alkyl morpholine catalyst. Basis for these claims is found in the working examples and again on page 20 of the specification. Such catalysts have not been disclosed heretofore and have many advantages over the heretofore available catalysts.

It is believed that the foregoing is a complete response to the Official Action and that each of the claims will be found allowable. Favorable reconsideration with early allowance of the claims is therefore earnestly solicited.

Respectfully submitted,

JAMES H. SAUNDERS
HERBERT L. HEISS

By Clelie W. Upchurch
Clelie W. Upchurch
Attorney for Applicants

Pittsburgh, Pennsylvania
January 23, 1958
CWU:gg

POL-99
Rev.
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THE COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications regarding
this application should give the
serial number, date of filing,
and name of the applicant.

PAPER No. 13

Clelle W. Upchurch
1815 Washington Road
Pittsburgh 34, Pa.

Please find below a communication from the
EXAMINER in charge of this application.

Robert Coston
Commissioner of Patents

Applicant:	James H. Saunders, et al
Ser. No.	373,036
Filed	August 7, 1953
For	NOVEL RESINOUS COM- POSITIONS AND METHOD OF PRODUCING SAME
MAILED	
FER 5 1958	
PAT DIV	

10-2247-4 000

Responsive to amendment of January 27, 1958.

The amendment of January 27, 1958 (Paper No. 12)

is deemed to be an incomplete response in that applicants have not complied with the requirements of Section 809.02(d) of the M.P.E.P. (2nd Edition). Applicants have presented various species claims, indicated infra, and have not made an ultimate election therefrom as required by the aforementioned section.

A) As to the foam inducing catalyst:

- (1) Alkali metal oxide
- (2) Calcium hydroxide
- (3) Benzyl trimethyl ammonium hydroxide

B) As to the non foam inducing catalyst

- (1) methyl-N-morpholine
- (2) ethyl morpholine

in each case

Applicants are required/(1) to elect a single disclosed species even though this requirement be traversed and (2) to list all claims readable thereon; including any claims subsequently added. Section 809.02(a) M.P.E.P.

Applicants must make a complete response within 20 days of the mailing date of the letter so as to avoid the possible question of abandonment.

DC

D. E. Czajakowski

G. H. Goston
Acting Examiner

Mo 918

FEB 7 1958

PAPER NO. _____
RECEIVED

FEB 24 1958

IN THE UNITED STATES PATENT OFFICE DIVISION 50

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

FILED: AUGUST 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS AND
METHOD OF PRODUCING SAME

DIVISION 50

AMENDMENT

The Honorable Commissioner of Patents
Washington 25, D. C.

Sir:

In response to the Official Action dated February 5, 1958, please amend the application as follows.

Claim 47, line 2, between "ethyl" and "morpholine",
insert -- N --.

REMARKS

Applicants elect to prosecute those claims directed to species A(1) and B(2). Claims 30 through 61 and Claim 63 read on the species A(1). Claims 58 through 61 and 63 are more specific than the remainder of the claims with respect to this species.

Claims 30 through 45, 47 and 48 through 66 read on the species B(2). Claim 47 has been amended to more clearly point out that the catalyst is ethyl-N-morpholine.

It is regretted that the Examiner considered the last Amendment incomplete and his indulgence in this matter is appreciated.

Respectfully submitted,
JAMES H. SAUNDERS
HERBERT L. WEISS

Pittsburgh, Pennsylvania
February 12, 1958
CWL/mn

By Cecile W. Weisz
Cecile W. Weisz
Attorney for Applicants

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Rev.
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WASHINGTON D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting
this application should give the
serial number, date of filing,
and name of the applicant.

PAPER NO. 15

Cleelle W. Upchurch
1815 Washington Road
Pittsburgh 34, Pa.

Please find below a communication from the
EXAMINER in charge of this application.

Robert Clinton
Commissioner of Patents.

<i>Applicant:</i> James H. Saunders, et al. (c)	
Ser. No.	373,036
Filed	August 7, 1953
For NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAME	
OCT 2 1958	

10-22487-4 6PC

Responsive to amendment of February 17, 1958.

Added art:

Windemuth	2,650,212	Aug. 25, 1953 (Filed Aug. 20, 1949)	260-2.5A
Detrick et al	2,787,601	Apr. 2, 1957 (Filed Mar. 3, 1953)	260-2.5A

"Chemical Engineering", Volume 57, No. 4, April, 1950, 260-2.5A
Pages 165 and 166. Copy in Scientific Library.

1. Claims 30 to 35 and 37 to 66 appear herein.
2. Claims 46, 62, 64 and 66 are withdrawn from further consideration as not readable upon the elected species. See Rule 142(b).

3. Claims 30 to 35, 37 to 45, 47 to 61, 63 and 65 are rejected as unpatentable over Rinke et al, Windemuth, Simon et al (2), Detrick et al and Chem. Eng. as set forth below.

The claims (30, 31, 32, 37, 48 to 50 and 55) which merely call for reacting an excess of an organic polyisocyanate with a compound having reactive hydrogen atoms or castor oil under substantially anhydrous conditions are unpatentable over any one of Rinke et al (example 1, for example). Windemuth et al (example 7, for example), Detrick et al (column 4, lines 55 to 75) or Chem. and Eng. News (page 166, column 2, lines 1-4) which show the above described reaction. To urge that Rinke et al

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disclose the reaction taking place in a solvent is of no moment since the omission of a component and its corresponding function from a procedure or a composition does not involve invention. Nothing critical is seen in carrying out the reaction at various temperatures as set forth in some claims, since said limitations do not appear in all the claims. Furthermore, Rinke et al disclose temperatures which are encompassed by the ranges set forth in the claims (see example 1).

The claims which call for a cellular polyurethane product (claims 40 and 41) are unpatentable over anyone of Windemuth (example 7), Simon et al (2) and Detrick et al, all of which show the same product. It is not seen wherein the use of a different catalyst makes for a product which is patentably distinct from that of the above cited prior art. Any difference in cell size, etc. would be considered to be a difference in degree only which is not a patentable distinction.

The claims which call for the use of "a non-foaming catalyst", viz.: a lower N-alkyl morpholine (claims 45 and 47) are unpatentable over Windemuth who discloses the use of various other tertiary amines (column 2, lines 43 to 52). It is the Examiner's opinion that applicants' catalysts are equivalent to the Windemuth catalysts. They are both used for the same purpose, viz: to render the reaction system more basic in nature. The increased basicity of the system will cause the reaction to proceed at a quicker rate.

The claims which call for the use of a "foaming catalyst" e.g. an alkali metal oxide (claims 58 to 60, 63 and 65) are unpatentable over Simon et al (2) who disclose the use of alkali metal hydroxides (examples 31 to 35, for example).

Again it is considered that applicants' catalysts are equivalent to the catalyst of Simon et al (2) since they are both used in a system where foam formation occurs and they both render the system more basic in nature so as to increase the rate of reaction. The claims do not exclude the water of Simon et al (2).

The claims which call for the use of an inert organic plasticizer having a boiling point above 200°C. (33, 34, 51 and 52) are unpatentable over Rinke et al who disclose the use of such a compound (paraffin oil - column 1, line 54 and example 23). The Rinke et al polyurethanes do not necessarily precipitate out (column 1, last line to column 2, line 3). Likewise, the claims which call for the use of the above plasticizer with castor oil as the reactive hydrogen compound or in the preparation of a cellular polyurethane wherein an alkali metal catalyst is used (claims 30, 43, 44, 57 and 61) are unpatentable over Rinke taken with Windemuth, Detrick et al, Simon et al and Chem. Eng. Windemuth, etc. disclose that it is old to prepare cellular resins from an excess of an organic polyisocyanate and a reactive hydrogen compound. Therefore, it would not involve invention to foam the polyurethane of Rinke et al via the use of the catalyst of Simon et al (2) or to use the castor oil of Detrick et al of Chem Eng. in lieu of the reactive hydrogen compounds of Rinke et al and foam the same.

No patentable distinction is seen in the use of a condensation product of an alkylene oxide and an organic tri-hydroxy compound (claims 35, 42, 53, 54 and 60) over the polyfunctional compounds of Rinke et al, Windemuth, Simon et al, Detrick et al and Chem. Eng.

Serial No. 373,036

-4-

4. Claims 30 to 35, 37 to 45, 47 to 61, 63 and 65 are rejected as being unduly multiplied. The presence of so many claims serve to obscure, rather than to point out the alleged invention. For example, no patentable distinction is seen between product-by-process claims 31 to 33 and 37 and between cellular product claims 40 and 41. In general, applicants are limited to only one product-by-process claim unless it can be shown that a patentable distinction exists between them.

5. Claims 35, 42, 53, 54 and 60 are rejected for lack of disclosure. There is nothing in the specification to indicate how the alkylene oxide-organic trihydroxy compound is prepared, that is, the conditions of reaction (temperature, pressure, catalyst, etc.). Nor is the molecular weight of the condensate set forth. Applicants are merely extending an invitation to the public to experiment and determine how to prepare the condensate and what molecular weight range is most desirable so as to obtain applicants' results.

6. Claims 45 and 65 are rejected as containing new matter in the phrases "an oxide of a metal of Group II of the Periodic Table" and "a lower alkyl-N-morpholine." There is nothing in the specification, as originally filed, to support the use of such language per se.

7. Claims 30 to 35, 37 to 45, 47 to 61, 63 and 65 are further rejected as failing to properly define the alleged invention. A) The phrase "R is an organic radical free from functional groups other than -NCX, urethane and thiourethane groups" (claims 30-34, 40-43, 48-52 and 58-60) is improper

Serial No. 373,036

-5-

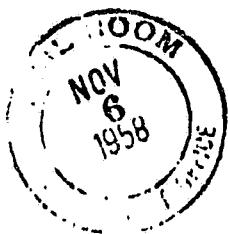
in that negative limitations should not be used in the claims. Applicants should define the compound in terms of what it is, rather than what it is not. B) The phrase "an organic compound having hydrogen atoms reactive with the said -NCX groups" (claims 30-34, 37, 40, 41, 43, 45, 48-52, 55, 58, 59 and 61) is too broad and indefinite. The phrase reads on sodium phenolate, hydroxylated polyethylene which have not been disclosed or contemplated by the applicants' as operative. C) All the claims are unduly broad in that the upper limit as to the amount of -NCX compound used is not set forth. The claims read on the use of very large excesses which would appear to yield undesirable results. D) The phrase "a catalyst which is an oxygen....precursors of such compounds" (claims 40-43 and 58-61) is unduly broad and indefinite. The use of such language is not warranted in view of the limited disclosure. The claims are also functional, and hence indefinite, since the compounds are defined in terms of their desired results. E) The phrase "tr...trihydroxy compound" (claims 35, 42, 53, 54 and 60) is too broad in that the molecular weight is not set forth. F) The claims containing the catalyst are unduly broad and indefinite in that the amount used is not set forth. It is not evident from the specification that any amount, e.g. 50 parts, would be operative. G) Claims 44 and 45 are indefinite in "effecting foaming" in that it is not stated how the reaction is effected. H) Claims 45 to 47 are indefinite in "N-morpholine." Accepted terminology is N-alkyl morpholine.

Serial No. 373,036

-6-

6. The specification is objected in that it is incomplete.
For reasons, see paragraph 5, supra.
9. No claim is allowed.
10. This rejection is made FINAL.


J. E. Cnajaskow
O'Brien
Examiner



PAPER NO. 16
RECEIVED
NOV 10 1958

IN THE UNITED STATES PATENT OFFICE DIVISION 50.

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

FILED: AUGUST 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS AND
METHOD OF PRODUCING SAME

letter

DIVISION 50

The Honorable Commissioner of Patents

Washington 25, D.C.

Sir:

An Office Action dated October 2, 1958, has been received in the above-identified application. The Examiner has finally rejected applicants' claims in this Office Action.

The Examiner is respectfully requested to reconsider the Final Rejection of the claims. It is submitted that the Final Rejection is premature and that reconsideration is in order as provided by Paragraph 706.07(d) of the "Manual of Patent Examining Procedure."

New references have been cited and relied upon in the Final Rejection. Moreover, claims have been rejected for the first time in this action on new grounds for rejection. Never before has the Examiner rejected claims such as Claims 45 and 47 as unpatentable over Windemuth. The alleged equivalency of applicants' catalyst to that disclosed by Windemuth raises a new issue. Moreover, applicants have not been provided with an

opportunity to remove references such as Detrick et al. by means of a Rule 131 affidavit.

Claims 30, 31, 32, 37, 48 to 50 and 55 have been rejected on three new references. New reasons are given for rejecting these claims.

It is applicants' position that the Final Rejection is premature because no clear-cut issues have been developed. It is, therefore, respectfully requested that the Final Rejection be withdrawn in order that applicants can reply to the Official Action and point out wherein their invention distinguishes patentably from these references.

Respectfully submitted,

JAMES H. SAUNDERS
HERBERT L. HEISS

By Clelie W. Upchurch
Clelie W. Upchurch
Attorney for Applicants

Pittsburgh, Pennsylvania
November 5, 1958
CWU/sm

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REV.
ADDRESS ONLY
THE CHIEF EXAMINER OF PATENTS
WASHINGTON 25, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting
this application should give the
serial number, date of filing,
and name of the applicant.

PAPER NO. 17

Cleelle W. Upchurch
1815 Washington Road
Pittsburgh 34, Pa.

Please find below a communication from the
EXAMINER in charge of this application.

Robert C. Watson
Commissioner of Patents.

Applicant: James H. Saunders, et al	
Ser. No. 373,036	MAILED RUV 25 1958 PAI 25 DIV
Filed August 7, 1953	
For NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAME	

16-6847-4 670

Responsive to letter of November 6, 1958.

Applicants request for withdrawal of the final
rejection has been carefully considered but is not granted.

Applicants through the presentation of new claims
presented issues which necessitated citing of new references,
etc. Accordingly, it is felt that the final rejection was
proper. See Ex parte Martin 104 U.S.P.Q. 124.

D. E. Chajakow
D. E. Chajakow

Ollieold
Examiner



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PAPER NO 18

RECEIVED

FEB 11 1959

DIVISION 50

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

FILED: AUGUST 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS AND
METHOD OF PRODUCING SAME

DIVISION 50

A M E N D M E N T

The Honorable Commissioner of Patents
Washington 25, D.C.

Sir:

In response to the Official Action dated October 21,
1958, please amend the application as follows.

Cancel Claims 30 through 34, 37 through 44, 48 through
52 and 54 through 66.

Claim 45, line 1, after "of" insert -- a cellular --;
same line, change "polyurethanes" to -- polyurethane --; line 2,
after "reacting" cancel "a" and before "compound" insert --
water, an excess of an --; same line, cancel "having the formula
 $R(NCX)_n$ "; same line, after "compound" insert -- selected from the
class consisting of an organic polyisocyanate and an organic
polyisothiocyanate --; line 3, cancel "having hydrogen atoms
reactive with $-NCX$, R in"; same line, after "compound" insert --
selected from the class consisting of a polyalkylene ether
alcohol having from 2 to 4 hydroxyl groups and having a molecular
weight of at least about 200 and castor oil --; line 4, cancel
"the said formula being an organic radical, X being selected

from"; line 5, cancel "the group consisting of oxygen and sulfur and n being an integer"; line 6, cancel "of at least 2,"; line 7, cancel "catalyst containing" and after "of a" insert -- catalytic amount of a --; same line, cancel "alkyl-N" and after "lower" insert -- N-alkyl --; line 8, between "morpholine" and the "period (.)" insert -- , said excess being at least 1.1 mols per mol --.

Claim 46, line 1, cancel "alkyl-N-" and after "lower" insert -- N-alkyl --; line 2, cancel "methyl-N-" and after "is" insert -- N-methyl --.

Claim 47, line 1, cancel "alkyl-N-" and after "lower" insert -- N-alkyl --; line 2, cancel "ethyl N" and before "morpholine" insert -- N-ethyl --.

Please add the following claims:

-- 67. The process of Claim 45 wherein the reaction is effected in the presence of from about 0.001 per cent to about 5 per cent by weight lower N-alkyl-morpholine.

68. A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) an hydroxy terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide having from 2 to 4 carbon atoms and about .01 to 10 mol per cent based on the alkylene oxide of a polyhydric alcohol having less than 7 carbon atoms and having 3 to 6 primary hydroxyl groups, at least 20 per cent of said alkylene oxide having more than 2 carbon atoms, and (2) at least about an equal molar amount of an organic diisocyanate based on said polyether glycol, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether glycol polymer is formed.

69. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of propylene oxide and about .01 to 10 mol per cent based on the propylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 6 hydroxyl groups, said condensation product having a molecular weight of at least 600 and (2) at least about one mol per mol of condensation product of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

70. A process of preparing a polyurethane reaction product comprising the steps of mixing (1) a liquid hydroxyl terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide of 2 to 4 carbon atoms inclusive, at least 20 per cent of said alkylene oxide having more than 2 carbon atoms and about .01 to 10 mol per cent based on the alkylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 6 hydroxyl groups and (2) at least an equal molar amount based on said condensation product of an organic polyisocyanate having 2 to 3 functional isocyanate groups, and reacting the mixture to form a reaction product having a chain length substantially greater than that of said polyether glycol polymer.

71. A product made according to process of Claim 68.

72. A product made according to process of Claim 70.

73. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a first polymer comprising a condensation product of about 100 parts by weight of propylene oxide and about .01 to 10 mol per cent based on the propylene oxide of pentaerythritol, said first polymer having a molecular weight of at least 600, and (2) at least about an equal molar amount based on the amount of said condensation product used of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said first polymer is formed.

74. A polyurethane reaction product of (1) about one mol of an organic diisocyanate and (2) about one mol of a condensation product of an alkylene oxide of 2 to 4 carbon atoms of which at least 15 per cent is propylene oxide, and about .01 to 10 mol per cent based on the alkylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 4 hydroxyl groups, said condensation product being hydroxy terminated and having a molecular weight of at least 600, said polyurethane reaction product having a chain length substantially greater than that of said condensation product.

75. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of a lower alkylene oxide and an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 6 hydroxyl groups, said condensation product having a molecular weight of at least 200, and (2) at least an equal molar amount based on said condensation product of an organic polyisocyanate having 2 to 3 functional isocyanate groups, and reacting the mixture to form a reaction product having a chain length substantially greater than that of said polyether glycol polymer. --

REMARKS

Reconsideration of the application in view of the foregoing amendments is respectfully requested. The recent interviews with the Examiner are acknowledged with appreciation.

The claims remaining in the application after this Amendment is entered can be divided into three groups: (1) Claims

45 through 47 and 67 which are directed to a process for making polyurethanes with an N-alkyl morpholine catalyst, (2) Claims 35, 53 and 75 which are directed to the preparation of a polyurethane by reacting a polyhydroxy compound prepared by condensation of an alkylene oxide with a polyhydric alcohol and (3) Claims 68 through 74 which were copied from U.S. Patent 2,866,774 for purposes of an interference and directed to an embodiment of the invention covered by Claims 35, 53 and 75. It was indicated at an interview that Claims 45 through 47 and 67 are allowable. Claims 35, 53 and 75 are believed allowable as well as Claims 45 through 47 and 67 but in the event they are not allowed, they place the application in better condition for an appeal so it is requested that the Amendment be entered for that purpose even though all the claims remaining in the application are not considered allowable.

As explained at the interview, it is counsel's opinion that the application is directed to more than one invention and several claims were presented in the last Amendment with the expectation of a requirement for restriction. Inasmuch as this point might be arguable and the attorney who filed the case felt that the application is directed to only one invention, counsel felt that he should have the Patent Office's opinion on this matter rather than file a divisional application on his own. However, no requirement for restriction was made so it has become necessary to cancel the claims directed to inventions which are clearly different from the invention encompassed by the uncancelled and newly presented claims. It is also counsel's opinion that Claims 45 through 47 and 67 are directed to an

invention which is distinct from that of Claims 35, 53 and 68 through 75. In view of the absence of a requirement for restriction and the issuance of U.S. Patent 2,866,774, it is believed necessary to retain Claims 45 through 47, 67 and 35, 53, 68 through 75 in this application unless restriction is required.

It is pointed out that Claims 45 through 47 and 68 are directed to the preparation of a polyurethane using an N-alkyl-morpholine catalyst with any organic compound having hydrogen atoms which will react with an organic polyisocyanate or poly-isothiocyanate to form a polyurethane. On the other hand, Claims 35, 53 and 68 through 75 are directed to the preparation of a polyurethane using any suitable catalyst. The novelty in this process is the use of a particular organic compound having reactive hydrogens, namely, broadly speaking, one prepared by condensing an alkylene oxide with a polyhydric alcohol.

Claims 45 through 47 were discussed in detail at a recent interview and it was pointed out that the rejection of these claims in the last Official Action is improper. These claims were rejected as unpatentable over Windemuth. An Affidavit of Paul O. Gemeinhardt, an established authority in the preparation of cellular polyurethanes, is presented herewith to show that applicants' catalyst is an improvement over those disclosed in Windemuth. Of all the catalysts disclosed by Windemuth, only triethylamine has met with any commercial success so this catalyst was chosen for the test. The Examiner will note from the Affidavit that the N-alkyl-morpholines are a decided improvement because the foam resulting from the reaction has improved tensile strength and improved compression set. Contrary to the

Examiner's opinion, the selection of a catalyst is not only to accelerate the reaction rate. The physical characteristics of foam are affected by the choice of catalyst so just any tertiary amine or similar alkylene compound cannot be used. The applicants devoted a considerable amount of time to the development of a catalyst and found that the N-alkyl-morpholines were superior to other catalysts for the preparation of foam in a system containing water.

No other reference was specifically applied against Claims 45 through 47 but it is pointed out that neither Rinke et al., Windemuth et al., Simon et al. (2), Detrick et al., nor "Chemical Engineering" discloses the N-alkyl-morpholine catalyst. None of these references indicates in any way that applicants' improved result of improved tensile strength and improved compression set would be obtained by the choice of catalyst in preference to one disclosed in these references.

Claims 45 through 47 have been amended to specify an excess of organic polyisocyanate or polyisothiocyanate. The formula considered undesirable by the Examiner has been deleted. The compound reacted with the isocyanate has been defined in a Markush group. The method of identifying the catalyst has been changed to conform with the procedure suggested by the Examiner. Claim 67 has been added to specify the preferred amount of catalyst set forth in the specification. The other claims require a catalytic amount of catalyst which is consistent with past practices and consistent with the disclosure.

As pointed out above, Claims 68 through 74 have been copied from U.S. Patent 2,866,774. An interference between Claims 1, 3, 4, 6, 8, 10 and 12 of the patent and Claims 68 through 74 is requested.

The relationship between the claims of this application and those of the patent is as follows:

<u>Claims of application</u>	<u>Corresponding claims of patent</u>
68	1
69	3
70	4
71	6
72	8
73	10
74	12

Applicants disclose each of the essential features of the above patent claims. Taking Claims 4, 8 and 12 of the patent as examples, Working Examples XI, XII, XIV, XV, XVII, lines 24 and 25 page 2, lines 5 through 12 page 5 and other portions of the specification show the preparation of a condensate meeting all the requirements set forth in (1) of the claims. A condensate prepared from 13.2 mols propylene oxide and 1 mol glycerine has a molecular weight of about 858 and thus meets the requirement "of at least 600". Propylene oxide meets the requirement of 2 to 4 carbon atoms in the alkylene oxide. The condensate is prepared from 100% propylene oxide in the above-listed working examples so the "at least 20 per cent" limitation is met. The mol percentage alkylene oxide is about 7.5% and within the range specified by the claims. Glycerine is an "aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 6 hydroxyl groups". The limitation under (2) of the claims is

met, inter alia, on page 3, last paragraph, the working examples, and page 5, second paragraph.

Each of the features of Claims 1, 3, 6, 8, 10 and 12 of the patent is also clearly disclosed in the application. Pentaerythritol, page 2, meets the limitation "primary hydroxyls" of Claims 1 and 6 and along with the working examples meets Claim 10. The other limitations of Claims 1 and 6 are disclosed in the references to the application made with respect to Claim 4.

The working examples clearly disclose the substance of Claim 3.

Annuet filiorum
The Examiner is referred to Den Beste vs. Martin 16 USPQ 584 for a case supporting applicants' position that they are entitled to a determination of priority.

It is submitted that applicants are entitled to allowance of Claims 35, 53 and 68 through 75. Claims 35 and 53 were rejected in the last Office Action as unpatentable over Rinke et al., Windemuth, Simon et al. (2), Detrick et al. and "Chemical Engineering". None of these patents disclose the process covered by these claims. It is pointed out that the references are just as effective against the claims of the Price patent as they are against applicants'.

Rinke et al. disclose a method for reacting diamines and glycols with a diisocyanate. They do not disclose a polyol prepared by condensation of an alkylene oxide with a polyhydric alcohol. Windemuth discloses the preparation of adhesives using a polyester. He does not disclose the reaction of the condensation product of an alkylene oxide and an alcohol with a

polyisocyanate. Likewise, Simon et al. (2) disclose the preparation of polyurethanes from polyesters and not from the condensation product of an alkylene oxide and an alcohol. Detrick et al. react a diisocyanate with a fatty acid glyceride. The alkylene oxide polyhydric alcohol condensate covered by the proposed claims is not mentioned in this patent. "Chemical Engineering" discloses the preparation of a polyurethane from castor oil and a diisocyanate. This reference is not at all pertinent to applicants' claims. There is nothing in these references which would lead to the conclusion that improved hydrophilic characteristics would be obtained if the condensate of the claims is used instead of a polyester. In view of this unexpected result, the subject matter is clearly patentable over the combination of any of the references.

The claims directed to the preparation of a polyurethane from the condensation product of an alkylene oxide and a polyhydric alcohol were rejected in the last Office Action for the first time and on the grounds that no method was disclosed for making the condensation product. Such products were not new compounds at the time the application was filed. Methods for making such compounds are disclosed in the art including, for example, in U.S. Patent 1,922,459. The processes disclosed in U.S. Patents 2,357,933 through 2,357,937 are also evidence that the skilled artisan could make applicants' condensation product as of the time applicants filed. It is not necessary for an applicant to disclose a method for making these compounds if they are known at the time he filed. The molecular weight is determinable from the proportions set forth in the specification including Examples 14, 15 and 17.

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The Examiner is requested to enter the Amendment, allow all the claims and declare an interference between the claims of the application and the Price patent as set forth above.

Respectfully submitted,

JAMES H. SAUNDERS
HERBERT L. HEISS

By Clellie W. Zschornak
Clellie W. Zschornak
Attorney for Applicants

Pittsburgh, Pennsylvania
February 4, 1959
CWU/sm

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PAPER NO. 15
REF ID: A

FEB 11 1959

DIVISION 50

IN THE UNITED STATES PATENT OFFICE

IN RE APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

FILED: AUGUST 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS AND
METHOD OF PRODUCING SAME

DIVISION 50

A F F I D A V I T

STATE OF West Virginia }
County OF Marshall } ss.

Now comes Paul G. Gemeinhardt, who being duly sworn, deposes and says that he is an organic chemist having received the degree of Bachelor of Arts with a major in Chemistry in 1950 from Central College of Fayette, Missouri; that he continued his studies in Chemistry at Northwestern University for one year thereafter; that he became an employee of the Monsanto Chemical Company on or about June, 1951, and immediately began working in research in the field of isocyanate chemistry; that he has continued during the following years to conduct and supervise research work relating to the preparation of polyurethane plastics and chemicals used in preparing such plastics; that he is presently employed by the Mobay Chemical Company as Group Leader in charge of the group of Mobay scientists conducting research work in the preparation of cellular polyurethane plastics; that he has had such position since on or about January, 1956; that in conjunction with other work dealing with the preparation of cellular polyurethanes, he has conducted

extensive tests to determine the most suitable catalyst for use in the preparation of cellular polyurethanes; that of all the various tertiary amine and other catalysts tried up to the time of filing the above-identified application including those disclosed in the Windemuth and other patents relied upon by the Examiner in rejecting Claims 45 through 47, N-ethyl morpholine and similar lower N-alkyl morpholines have met with the most success and the widest commercial application in the preparation of cellular polyurethanes from a reaction mixture containing water; that he is aware of the research work of Dr. James H. Saunders and Herbert L. Heiss which resulted in the invention described and claimed in the above-identified application; that research work conducted by him and under his supervision since the filing of the said application has consistently brought out that N-ethyl morpholine and similar lower N-alkyl morpholines are advantageous over the catalysts used and known at the time of the filing of the above-identified application; that in a recent test, N-ethyl morpholine was used in the preparation of a cellular polyurethane in comparison with triethylamine, one of the catalysts disclosed in the Windemuth Patent 2,650,212; that in this test, a cellular polyurethane was prepared under identical conditions and while using identical manipulative steps and identical chemicals with the exception that N-ethyl morpholine was used as the catalyst in one experiment and triethylamine was used in the other experiment; that in the preparation of cellular polyurethanes in these experiments, about 100 parts by weight of an -NCO terminated prepolymer (prepared by reaction of about 36 parts toluylene diisocyanate with about 60 parts polypropylene ether glycol having a molecular weight of about 2,000 and about 40 parts triol prepared by condensing propylene oxide and

glycerine and having a molecular weight of about 3,000) were reacted with about 2.5 parts by weight water in the presence of about 4 parts N-ethyl morpholine in one experiment and about 4 parts triethylamine in the other experiment; that it was found that the reaction mixture containing the N-ethyl morpholine foamed and set into a cellular polyurethane having a tensile strength of about 22.4 pounds per square inch and a compression set of about 4.5 per cent while the reaction mixture containing the triethylamine foamed and set into a cellular polyurethane having a tensile strength of about 15.8 pounds per square inch and a compression set of 32 per cent; that the compression set value is determined by compressing a block of cellular polyurethane to 50 per cent of its original thickness for 22 hours at 158°C., then permitting it to recover for 30 minutes at room temperature; the difference in thickness of the block before compression and after the 30-minute recovery period expressed as percentage of the original thickness being the compression set value; that the lower value of 4.2 per cent compression set is far superior to the value obtained when triethylamine is used because it permits stacking of slabs of cellular polyurethane one on another immediately after they are formed and permits handling of the cellular polyurethane substantially immediately after it has been formed; that in addition to the advantageous characteristics of tensile strength and compression set, it has also been found possible to vary the load-bearing characteristics of the cellular polyurethane to a greater extent when using N-ethyl morpholine than when using triethylamine and that this characteristic is advantageous particularly when it is desired to

prepare a cellular polyurethane of a particular firmness for use in cushioning, mattresses and the like; that he is familiar with the rejection of Claims 45 through 47 on the Examiner's opinion that the N-alkyl morpholine catalysts are equivalent to the Windemuth catalysts and that the Examiner is in error in this conclusion because as is exemplified by the data above an improved product is obtained with the N-alkyl morpholines; and that the purpose of the catalyst in preparing cellular polyurethanes is not solely to render the reaction system more basic and thus accelerate the reaction rate.

Further Deponent sayeth not.

Paul G. Gemeinhardt
Paul G. Gemeinhardt

Before me personally appeared Paul G. Gemeinhardt to me known to be the person who signed the foregoing Affidavit in my presence this 29th day of December, 1958

D. J. Dutton, Jr.
Notary Public

My commission expires _____
My Commission begins July 1, 1963

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U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON 25, D. C.

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U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting
this application should give the
serial number, date of filing,
and name of the applicant.

Paper No. 19

Clelie W. Upchurch
1815 Washington Rd.
Pittsburgh 34, Pa.

Applicant:	
James H. Saunders et al.	
Ser. No.	373,036
Filed	Aug. 7, 1953
For NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAE	
MAILED MAR 5 1959 PAUL J. COOPER P.M. 3	

Please find below a communication from the
EXAMINER in charge of this application.

Robert Clinton
Communication of Patent

Responsive to amendment filed Feb. 6, 1959

Cited as a teaching reference:

Reis 2,779,689 Jan. 29, 1957 260/2.5A

1. The proposed amendment of February 6, 1959

(Paper No. 18) has not been entered since it does not place
the case in condition for allowance.

2. Claims 45 to 47 stand rejected and proposed
claim 67 would be rejected as unpatentable over Windemuth of
record for the reasons set forth in paragraph 3 of the final Office
action (Paper No. 15) and Reis, newly cited as a teaching reference.

The affidavit has been considered but is deemed not
to overcome the above rejection. The Examiner is still of the
opinion that the claimed N-alkyl morpholine catalysts are
equivalent to the catalysts of Windemuth, viz. triethyl amine.
The art as evidenced by Reis considers the N-alkyl morpholines
as being equivalent to triethyl amine. See column 5, lines
1 to 10 of Reis. Applicants disclose the above catalysts as
equivalents. See page 20, lines 1 to 13. It is not seen wherein
the Gemeinhardt affidavit disproves the teaching of equivalency.
The alleged non-equivalency is predicated upon the fact that the
N-alkyl morpholines yield cellular products which have improved

tensile strength, compression set and load bearing characteristics. None of these features were disclosed in the specification as originally filed. Accordingly, applicants cannot use said features as the basis of patentability. See In re Crawford 727 O. G. 2; In re Dalzell, 77 U.S.P.Q. 164 and Abbott et al v. Coe 43 U.S.P.Q. 267.

The affidavit is also improper in that the exact amount of catalyst used is not set forth. For example "about 4 parts N-ethyl morpholine" can read on 3.6 parts and "about 4 parts of triethylamine" can read on 4.4 parts.

Furthermore, specification at page 20, lines 7 to 10, states that N-alkyl morpholines in order to be effective must be used in conjunction with other disclosed catalysts, eg. sodium hydroxide, etc. The claims as they presently stand read on the use of the morpholines alone. Likewise, the affidavit shows the use of N-ethyl morpholine alone. Moreover, it is not seen wherein the use of the morpholine catalyst alone would yield a cellular product since water is not present which is necessary for the foaming reaction. The specification makes no mention of water, which is present in the examples of the affidavit. No patentable distinction is seen between applicants' active hydrogen compounds, viz: castor oil and the "alkylene ether alcohol" and the polyester of Windemuth since they are old in the art as shown by Detrick et al and Chem. and Eng. News. Accordingly, to use the tertiary amine catalyst of Windemuth in a castor oil-polyisocyanate foaming system would not involve invention.

3. If the above amendment were entered claim 45 would be rejected as containing new matter. There is no basis in the specification for the insertion of the term "water" and

the phrase "a polyalkylene ether alcohol having from 2 to 4 hydroxyl groups".

4. If the above amendment were entered claim 45 would also be rejected as failing to properly define the invention. The phrase "a polyalkylene ether alcohol---4 hydroxyl groups" is too broad and indefinite. Applicants have not disclosed any specific compounds to support the ether glycols having 3 to 4 hydroxyl groups. "Said excess being at least 1.1 moles per mole". Per mol of what? Further, the disclosure at page 5, the ratio is described in terms of the reactive groups.

5. Claims 35 and 53 stand rejected and proposed claim 75 would be rejected as failing to properly define the invention. The claims are too broad and indefinite in "alkylene oxide" "organic trihydroxy compound", "lower alkylene oxide" and "an aliphatic polyhydric alcohol---to 6 hydroxyl groups". For example, the oxide reads on butylene, hexylene oxides, etc.; "organic trihydroxy compound" reads on cholic acid and "an aliphatic polyhydric alcohol" reads on mannitol, sorbitol, etc. all of which haven't been disclosed or contemplated by the applicants as operative for their purposes.

6. If the above amendment were entered, proposed claim 75 would be rejected as containing new matter in the phrases: "an aliphatic polyhydric alcohol---to 6 hydroxyl groups... 3 functional isocyanate groups". There is no basis in the specification for such terminology as originally filed.

7. Proposed claims 69 to 74 cannot be entered for purposes of interference since they are not patentable to applicants. That is to say: there is no support for the phrases: "An alkylene oxide having from 2 to 4 carbon atoms" since only

ethylene and propylene oxide are disclosed; "a polyhydric alcohol---3 to 6 primary hydroxy groups" since only pentaerythritol is disclosed. Likewise, the disclosure does not support the ranges set forth in the claims, namely mole ratio of oxide to alcohol and mole ratio of polyisocyanate to the polymer. For example, applicants must always have an excess of polyisocyanate. Further, the sole disclosure of glycerol and pentaerythritol does not support the broad language "an aliphatic alcohol---3 to 6 hydroxyl groups". See *In re Rogoff* 733 U. S. 808.

6. The following claims, found allowable are suggested for purposes of interference. Applicants should make same within 30 days of the mailing date of this letter under the provisions of Rule 203; failure to do so will be considered a disclaimer of the subject matter involved:

Suggested Claims

A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of propylene oxide and about ~~0.075 to 0.33 mol~~ 7.5 to 10 per cent based on the propylene oxide of an aliphatic polyhydric alcohol of less than 6 carbon atoms and having from 3 to 4 hydroxyl groups and (2) at least about $1\frac{1}{2}$ moles per mole of condensation product of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

A process of forming a polyurethane reaction product comprising the steps of mixing (1) a first polymer comprising a condensation product of about 100 parts by weight of propylene oxide and about ~~0.075 to 0.33 mol~~ 7.5 to 10 percent based on the propylene oxide of pentaerythritol, and (2) at least about 2 moles based on the amount of said condensation product used of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of the first polymer is formed.

Should applicants make the above suggested claims, then an interference will be declared between the Price Patent and the instant application with claims 3 and 10 of the patent

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Serial No. 373,036

- 5 -

constituting the counts of the interference, and with the proviso that there is no patentable distinction between the suggested claims and the counts of the interference.

9. Attention is directed to the provisions of Section 1101.01(n) of the M.P.E.P. and Rule 203(c) of the Rules of Practice.

DR
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Oliver
Examiner

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PAPER NO. 20/E
RECEIVED
MAR 27 1959
DIVISION 50

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

FILED: August 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS AND
METHOD OF PRODUCING SAME

DIVISION 50

AMENDMENT AFTER FINAL REJECTION

The Honorable Commissioner of Patents

Washington 25, D. C.

Sir:

In response to the Official Action dated March 5, 1959,
please add the following claims.

-- 76. A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) a hydroxy terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide having from 2 to 3 carbon atoms and from about 7.5 to about 10 mol per cent based on the alkylene oxide of a polyhydric alcohol having less than 7 carbon atoms and having 3 to 4 primary hydroxyl groups, at least 20 per cent of said alkylene oxide having more than 2 carbon atoms, and (2) at least about 1 1/2 mols per mol of an organic diisocyanate based on said polyether glycol, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether glycol polymer is formed.

77. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of propylene oxide and about 7.5 to 10 mole per cent based on the propylene oxide of an aliphatic polyhydric alcohol of less than 6 carbon atoms and having from 3 to 4 hydroxyl groups and (2) at least about 1 1/2 moles per mole of condensation product of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

78. A process of preparing a polyurethane reaction product comprising the steps of mixing (1) a liquid hydroxyl terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide of 2 to 3 carbon atoms inclusive, at least 20 per cent of said alkylene oxide having more than 2 carbon atoms and about 7.5 to about 10 mol per cent based on the alkylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 4 hydroxyl groups and (2) at least about 1.1 mols per mol of said condensation product of an organic polyisocyanate having 2 to 3 functional isocyanate groups, and reacting the mixture to form a reaction product having a chain length substantially greater than that of said polyether glycol polymer.

79. A product made according to process of Claim 76.

80. A product made according to process of Claim 78.

81. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a first polymer comprising a condensation product of about 100 parts by weight of propylene oxide and about 7.5 to 10 mole per cent based on the propylene oxide of pentaerythritol, and (2) at least about 2 moles based on the amount of said condensation product used of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of the first polymer is formed.

82. A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of propylene oxide and about 7.5 to 10 mole per cent based on the propylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 4 hydroxyl groups and (2) at least about 1 1/2 moles per mole of condensation product of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

REMARKS

The recent interview with the Examiner is acknowledged with appreciation. The following remarks embody all that transpired at the interview.

Claims 77 and 81 are the claims suggested by the Examiner for the purposes of an interference with Claims 3 and 10 of the Price patent 2,866,774. Claim 82 is exactly like Claim 77 with the exception that the polyhydric alcohol has less than 7 carbon atoms instead of less than 6. Triethanol amine is disclosed on page 3, line 5, which provides a basis

for less than 7 carbon atoms. It is submitted that the interference should be declared between Claim 3 of the Price patent and Claim 82 instead of Claim 77.

It is submitted that an interference should also be declared between each of the following claims of this application and the corresponding claim of the Price patent:

<u>Applicants' Claims</u>	<u>Claims of Price Patent</u>
76	1
78	4
79	6
80	8

Applicants have followed the Examiner's lead in writing Claims 76 and 78 through 80. The range of mol per cent of polyhydric alcohol based on the alkylene oxide is about 7.5 to about 10 which is the same as that in the claims suggested by the Examiner.

An interference should be declared between applicants' Claim 76 and Claim 1 of the Price patent because the claim is patentable to applicants and is directed to substantially the same subject matter as the claim of the patent. The Examiner objected to a claim setting forth "an alkylene oxide having from 2 to 4 carbon atoms". Accordingly, the claim now specifies 2 to 3 carbon atoms. Applicants' disclosure supports this range.

Applicants have not limited the number of carbon atoms in the polyhydric alcohol to less than 6 because they have a basis for less than 7 carbon atoms. The Examiner is referred

to page 3, line 5, where applicants disclose triethanolamine as one of the alcohols to be condensed with the alkylene oxide. Triethanolamine and pentaerythritol provide a basis for from 3 to 4 primary hydroxyl groups on the polyhydric alcohol.

As pointed out in the previous amendment, applicants use of 100% propylene oxide provides a basis for at least 20% of the alkylene oxide having more than 2 carbon atoms. The mol per cent of organic diisocyanate suggested by the Examiner in the proposed claims has been adopted in this claim. It is believed obvious from the foregoing that Claim 76 should be placed in interference with Claim 1 of the Price patent.

Claim 78 is proposed for purposes of interference with Claim 4. It has been shown above with respect to Claim 76 that applicants have a basis for the limitations of from 2 to 3 carbon atoms in the alkylene oxide, at least 20% alkylene oxide having more than 2 carbon atoms, less than 7 carbon atoms in the polyhydric alcohol and from 3 to 4 hydroxyl groups. This claim requires 1.1 mols polyisocyanate per mol of condensation product because this is consistent with applicants' disclosure. In Claim 78 and in Claim 4 of the Price patent the isocyanate is an organic polyisocyanate having 2 to 3 functional groups. Applicants have disclosed in their specification, page 5, a range of -NCX groups to active hydrogen atoms beginning at 1.1 to 1. If the organic polyisocyanate has 3 isocyanate groups and a 1.1 ratio is used, 3.3 -NCO groups per mol of trihydric compound would be required which is equivalent to 1.1 mol triisocyanate per mol trihydric compound.

Claims 79 and 80 are dependent claims and the subject matter thereof is substantially the same as that of Claims 6 and 8, respectively, of the Price patent.

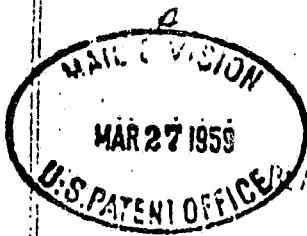
An early declaration of an interference is requested.

Respectfully submitted,

JAMES H. SAUNDERS
HERBERT L. HEISS

By Clelle W. Upchurch
Clelle W. Upchurch
Attorney for Applicants

Pittsburgh, Pennsylvania
March 23, 1959
CWU:as



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APR 1 1959
U. S. PATENT OFFICE

APPEAL NO. 342-05

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

FILED: August 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS AND
METHOD OF PRODUCING SAME

DIVISION 50

APPEAL
TO
BOARD OF APPEALS

The Honorable Commissioner of Patents

Washington 25, D. C.

Sir:

Applicants hereby appeal to the Board of Appeals from
the decision of the Examiner finally rejecting Claims 30 to 35
and 37 to 66.

The enclosed check for \$25.00 covers the Appeal Fee.

Respectfully submitted,

JAMES H. SAUNDERS
HERBERT L. MEISS

By Clelle W. Upchurch
Clelle W. Upchurch
Attorney for Applicants

Pittsburgh, Pennsylvania
March 26, 1959
CWU:ma

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INTERFERENCE

Interference No. 90414

Paper No. 22

Names: James H. Saunders and Herbert L. Heiss

Serial No. 373,036..... Patent No.

TITLE. NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAME

Filed, August 7, 1953.

Interference with Charles G. Price

DECISION ON MOTIONS

Primary Examiner. _____ *Dated,* _____

DECISIONS ON PRIORITY

Board of Interference Examiners, Adverse Dated, Mar 23/62

Court, Dated,

REMARKS

This should be placed in each application or patent involved in interference in addition to the interference letters by Primary Examiner.

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Forwarded to the Exr. of Interferences
from Division

MAY 6 1959

All communications respecting
this application should give the
serial number, date of filing,
and name of the applicant.

POL-76

ADDRESS ONLY
THE CHIEF EXAMINER OF PATENTS
WASHINGTON 25, D. C.

Czajak:kmw

DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE
WASHINGTON

PAPER NO.

23

Cleelle W. Upchurch
1815 Washington Road
Pittsburgh 34, Pa.

Please find below a communication from the
EXAMINER in charge of this application.

Robert Clinton
Commissioner of Patents

The case referred to above is forwarded to the Examiner of Interferences because it is adjudged to interfere with other cases hereafter specified. The question of priority will be determined in conformity with the Rules of Practice. The interference will be identified as No. 90414

On or before AUG 24 1959 the preliminary statement demanded by Rules 215 et seq. must be filed in a sealed envelope bearing the name of the party filing it and the number and title of the interference. The subject matter involved in the interference is presented in claims 82, 81, 76, 78, 79, and 80 of this application.

The interference involves your application above identified and:

A patent for POLYETHER POLYURETHANE RUBBER granted December 30, 1958, No. 2,866,774, on application filed September 23, 1953, No. 381,999 by Charles C. Price, whose post-office address is 201 West North Drive, South Bend, Indiana, whose attorneys are McCoy, Greene & TeGrotenhuis, Bulkley Building, Cleveland 15, Ohio, and whose assignee is University of Notre Dame, Notre Dame, Indiana, a non-profit Institution.

The relation of the counts of the interference to the claims of the respective parties is as follows:

Count	Price	Saunders et al
1	3	82 (modified)
2	10	81 (modified)
3	1	76 (modified)
4	4	78 (modified)
5	6	79 (modified)
6	8	80 (modified)

Serial No. 373,036

-2-

After termination of the interference this application will be held subject to further examination under Rule 266.

Claims 35 and 53 will be held subject to rejection as unpatentable over the issue in the event of an award of priority adverse to applicants.

Count 1

A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of propylene oxide and about .01 to 10 mol percent based on the propylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 6 hydroxyl groups, said condensation product having a molecular weight of at least 600 and (2) at least about one mole per mol of condensation product of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

Count 2

A process of forming a polyurethane reaction product comprising the steps of mixing (1) a first polymer comprising a condensation product of about 100 parts by weight of propylene oxide and about .01 to 10 mol percent based on the propylene oxide of pentaerythritol, said first polymer having a molecular weight of at least 600, and (2) at least about an equal molar amount based on the amount of said condensation product used of an organic diisocyanate, and reacting the mixture until a second polymer having a chain length substantially greater than that of said first polymer is formed.

Count 3

A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) a hydroxy terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide having from 2 to 4 carbon atoms and about .01 to 10 mol percent based on the alkylene oxide of a polyhydric alcohol having less than 7 carbon atoms and having 3 to 6 primary hydroxyl groups, at least 20 percent of said alkylene oxide having more than 2 carbon atoms, and (2) at least about an equal molar amount of an organic diisocyanate based on said polyether glycol, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether glycol polymer is formed.

Count 4

A process of preparing a polyurethane reaction product comprising the steps of mixing (1) a liquid hydroxyl terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide of 2 to 4 carbon atoms inclusive, at least 20 percent of said alkylene oxide having more than 2 carbon atoms and about .01 to 10 mol percent based on the alkylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 6 hydroxyl groups and (2) at least an equal molar amount based on said condensation product of an organic polyisocyanate having 2 to 3 functional isocyanate groups, and reacting the mixture to form a reaction product having a chain length substantially greater than that of said polyether glycol polymer.

Count 5

A product made according to process of count 3.

Count 6

A product made according to process of count 4.


Counts compared.

122
122


Orrud 93
Examiner

7/24

RECEIVED
MAY 14 1959
FIRST ASSISTANT COMMISSIONER
IN THE UNITED STATES PATENT OFFICE

In re the Application of
JAMES H. SAUNDERS et al
Serial Number 373,036
Filed: August 7, 1953
For: NOVEL RESINOUS COMPOSITIONS
AND METHODS OF PRODUCING SAME

On Appeal from Div. 50
(Appeal No. 24,205)

PETITION FOR EXTENSION OF TIME
FOR FILING BRIEF ON APPEAL

Now come the appellants, by their attorney, and respectfully petition the honorable Commissioner of Patents for a 62-days' extension of time for filing the brief on appeal, i.e., from Tuesday, May 26, 1959, the date now set, until Monday, July 27, 1959, but without affecting the date of hearing and consequently the date of final disposition of the case in the Patent Office.

The facts upon which this petition is based are as follows:

The application was finally rejected on October 2, 1958 and a formal Notice of Appeal was filed on March 27, 1959. An amendment copying claims was filed on March 24, 1959 in response to an Office Action dated March 5, 1959 which suggested claims for purposes of interference.

It is understood that the Examiner of Division 50 has forwarded the application to the Interference Division for purposes of declaring the interference, but in a telephone conversation this morning with an employee of the Interference Docket

Extension of time
by _____
1959

Arthur W. O'Dell

Branch it was learned that it might require two weeks or more before the formal declaration of interference can be actually sent out.

When that is done then of course ex parte proceedings are suspended (Rule 212) and hence the actual mailing of the declaration of interference before the brief is due to be filed might save much time and energy on the part of the Patent Office, in that the brief, when and if it is required after the termination of the interference, can then be written in the light of the then posture of the case.

Under these circumstances, it is believed that this extension of time is necessary in order to provide additional time to permit the Interference Division of the Patent Office to attend to the details of formally declaring the expected interference.

It is hereby certified that this petition is made in good faith for the reasons indicated above, and not solely for purposes of delay.

Respectfully submitted,

Clelie W. Upchurch
Clelie W. Upchurch
Attorney for Appellant

May 14, 1959

#25

U. S. DEPARTMENT OF COMMERCE

PATENT OFFICE

WASHINGTON 25, D. C.

May 15, 1959

COMMISSIONER'S OFFICE

In re application of :
James H. Saunders et al :
Serial No. 373,036 : Request to Extend Time
Filed August 7, 1953 : for Brief on Appeal
For: Novel Resinous Com- : Appeal #242-05
positions and Method of :
Producing Same

Sir:

The decision of the First Assistant Commissioner on the petition filed in the above entitled application is as follows:

- Delay in Prosecution Held Unavoidable (35 U.S.C. 133),
Petition Granted _____
- Approved _____
- Delayed Payment of Final Fee Accepted (35 U.S.C. 151),
Petition Granted _____
- Extension of Time to July 27, 1959 Granted May 15, 1959
- Petition Granted _____
- Petition Denied _____

By direction of the
First Assistant Commissioner:

Alfred P. Bayless

Clelio W. Upchurch
1815 Washington Road
Pittsburgh 34, Pa.

125

MAILED

Appeal No. 242-05

JUL 30 1959

law

U. S. Patent Office
Board of Appeals
IN THE UNITED STATES PATENT OFFICE

BEFORE THE BOARD OF APPEALS

Ex parte James H. Saunders
and Herbert L. Heiss

- - -

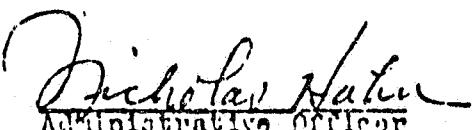
Application for Patent filed August 7, 1953, Serial
Number 373,036. Novel Resinous Compositions and Method
of Producing Same.

Elmer P. Rucker, F. M. Murdock, Donald J. Haefele and
Clelle W. Upchurch for appellants.

In view of the declaration of an interference, Number
90414, since the filing of Appeal Number 242-05, proceedings
before the Board are hereby suspended pending termination of
the interference at which time the appeal should be called
up for action by filing the brief not later than sixty (60)
days from date interference terminates.

By Order of the Board of Appeals.

oc
Clelle W. Upchurch
1815 Washington Road
Pittsburgh 34, Penna.


Nicholas Natale
Administrative Officer

DOCKET DIVISION
 SEP 15 1959
 U. S. PATENT OFFICE

90414

IN THE UNITED STATES PATENT OFFICE

277
 7
 Affidavit
 HL

In re the Application of

JAMES H. SAUNDERS ET AL.

Serial No. 373,036

Division 50

Filed: August 7, 1953

Title: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAMEAMENDMENTThe Hon. Commissioner of Patents,
Washington 25, D. C.

Sir:

Please enter the following amendment: / / /
 Cancel all of the claims except claims 35, 53, 54,
 76 and 78 - 82.

It is also requested that the application be remanded
to the Primary Examiner for consideration of the enclosed papers
under rule 45. As is apparent from the accompanying Affidavit
it has become apparent that the invention covered by the claims
remaining in the application after this amendment is entered, is
the sole invention of Herbert L. Heiss. The Primary Examiner is,
therefore, requested to delete the names of James H. Saunders
from the application, as provided for by rule 45.

Respectfully submitted,

JAMES H. SAUNDERS
HERBERT L. HEISS

By Cecilie W. Upchurch
 Cecilie W. Upchurch
 Attorney for Applicants

Pittsburgh, Pennsylvania
 September 11, 1959
 CWU:rdo

Mo 218

637a

27

IN THE UNITED STATES PATENT OFFICE**APPLICATION OF**

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

FILED: August 7, 1959

TITLE: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

DIVISION 50

AFFIDAVIT

James H. Saunders and Herbert L. Heiss, being duly sworn, depose and say that they are the joint applicants who filed the above-identified application on August 7, 1953; that prior to the filing of the said application, affiants were engaged in a joint research program relating to the preparation of polyurethane plastics and chemicals useful for making polyurethane plastics; that laboratory work was being conducted by them and under their direction at that time; that they frequently discussed the results of such laboratory work while jointly making plans for further investigating the preparation of polyurethane plastics from organic polyhydric compounds and organic polyisocyanates; that all of the subject matter of the above-identified application was conceived and reduced to practice during this joint program; that all laboratory results and other information pertinent to all of the subject matter of the application considered by them to be required by an attorney for patent consideration were submitted to their attorney; that the attorney concluded from the information furnished him that affiants were joint inventors of all of the subject matter of the application; that after the declaration of Interference 90,414, affiants made their records relating to all

the subject matter of the application available to the attorney presently handling the application; that it is apparent from these records including some not made available to the other attorney that affiants are joint inventors of some but not all of the subject matter described in the application, and that the invention covered by Claims 35, 53, 54, 76, and 78 through 82 is the sole invention of Herbert L. Heiss; that it is now apparent that an error was made at the time the application was filed and that the name of James H. Saunders should be deleted as an inventor of the subject matter being claimed in the application after the accompanying Amendment is entered; that the error was accidental and inadvertent and without any fraudulent intent; and that steps are being taken promptly after discovery of the mistake to delete the name of James H. Saunders from the application.

Further Deponent sayeth not.

State of West Virginia }
 County of Mars Hill } SS:

James H. Saunders
 James H. Saunders

Herbert Heiss
 Herbert L. Heiss

Subscribed and sworn to before me this 11th day of
September, 1959.

SEAL

A. Clegg J. Fifer
 Notary Public

My Commission Expires

639a

OATH

Herbert L. Hoiss, being sworn, deposes and says that he is a citizen of the United States of America and resident of Route 1, Cider Run, New Martinsville, West Virginia, that on August 7, 1953, he filed application for patent Serial No. 373,036 in the United States Patent Office, that he verily believes himself to be the original, first and sole inventor of as much of the improvement in NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAME described in the specification of said application for patent as is the subject matter of claims 35, 53, 54, 76, and 78 through 82; ¹¹ that he does not know and does not believe that the same was ever known or used before his invention thereof, or patented or described in any printed publication in any country before his invention thereof, or more than one year prior to the date of said application, or in public use or on sale in the United States more than one year prior to the date of said application; that said invention has not been patented before the date of said application in any country foreign to the United States on an application filed by him or his legal representatives or assigns more than twelve months prior to the date of said application; and that no application for patent on said invention has been filed by him or his representatives or assigns in any country foreign to the United States, except as follows:

Australia, filed August 5, 1954; Canada, filed February 27, 1954;
Germany, filed April 12, 1954; and Great Britain, filed August 6, 1954.

Inventor

Herbert L. Heiss

Post Office Address

Route 1, Cider Run

New Martinsville, West Virginia

State of West Virginia }
County of Martinsville } SS:

Sworn to and subscribed before me this 11th day of

September, 1959.

SEAL

Daniel T. Price
Notary Public

My Commission Expires

POL-90
Rev.
ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

641a

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communication respecting
this application should give the
serial number, date of filing,
and name of the applicant.

PAPER No. 28

Clelle W. Upchurch
1815 Washington Road
Pittsburgh 34, Pa.

Please find below a communication from the
EXAMINER in charge of this application.

Robert Chester
Commissioner of Patents.

Applicant:	James H. Saunders, et al
Ser. No.	373,036
Filed	August 7, 1953
For	NOVEL RESINOUS COM- POSITIONS AND METHOD OF PRODUCING SAME
EX-141959	
10-2467-6 28	

Responsive to amendment of September 15, 1959.

The amendment of September 15, 1959 (Paper No. 27)
proposing to convert the instant application from joint
inventorship to sole inventorship has not been entered.

Applicants allegations are considered to be insufficient.
Rule 45(b) requires that a verified statement of facts
must be presented. The affidavit of Saunders and Heiss
does not contain such a statement of facts but general con-
clusions. For example, affiants state that it is apparent
from certain records that they are not joint inventors.
The records affiants speak of are not of record in the
instant case as facts so as to enable one to make a proper
determination as to whether the conversion from joint to
sole is proper.

D. E. Czajaskow
D. E. Czajaskow

O'Driscoll
Examiner

642a

POL-98
Rev.
ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications regarding
this application should give the
Serial number, date of filing,
and name of the applicant.

Clelle W. Upchurch
1815 Washington Road
Pittsburgh 34, Pa.

Please find below a communication from the
EXAMINER in charge of this application.

Robert C. Watson
Commissioner of Patents

PAPER NO. 29

Applicant:	James H. Saunders, et al
Ser. No.	3,73,036
Filed	August 7, 1953
for NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAME	
MAILED OCT 20 1953	
PAID 50	

This action is supplemental to the Office letter
of October 14, 1959.

In order to clear the record and thereby expedite
the proceedings in Interference No. 90,414, a SHORTENED
PERIOD FOR RESPONSE TO THE OFFICE LETTER OF OCTOBER 14, 1959
IS SET TO EXPIRE NOVEMBER 16, 1959.

D. E. Czajaskew

Examiner

643a

Mo 218



PAPER NO. 30

NOV 19 1959

Letter &
affidavits

REG'D. USPO

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF

JAMES H. SAUNDERS ET AL

SERIAL NO. 373,036

FILED: August 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

DIVISION 50

The Honorable Commissioner of Patents

Washington 25, D. C.

Sir:

Enclosed herewith are affidavits signed by James H. Saunders and Herbert L. Weiss. It is believed that these affidavits are free from the objections set forth in the Official Action dated October 14, 1959.

Respectfully submitted,

JAMES H. SAUNDERS
HERBERT L. WEISS

By Cleelle W. Upchurch
Cleelle W. Upchurch
Attorney for Applicants

Pittsburgh, Pennsylvania
CWU:rdo
November 9, 1959

MAIL ROOM
NOV 16 1959
PAPER NO. 30
RECEIVED

NOV 19 1959

DIVISION 50

REC'D 19 1959

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

DIVISION 50

FILED: AUGUST 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME)AFFIDAVIT OF JAMES H. SAUNDERS

James H. Saunders, being duly sworn, deposes and says that he is one of the joint applicants who filed the patent application Serial No. 373,036 on August 7, 1953; that prior to the filing of the said application, affiant and his co-applicant Herbert L. Heiss were engaged in a joint research program relating to the preparation of polyurethane plastics; that a large part of the research work conducted prior to the filing of the said application and relating to the preparation of polyurethane plastics was done jointly with the co-applicant Herbert L. Heiss; that he has read the Amendment filed September 15, 1959, in patent application Serial No. 373,036 and that he understands that upon the entry of this Amendment by the Patent Office the only claims remaining in the application will be Claims 35, 53, 54, 76 and 78 through 82; that affiant understands that these claims are directed to a method for making a polyurethane comprising reacting an organic polyisocyanate and a polyalkylene ether prepared by condensation of an alkylene oxide with a polyhydric alcohol including an embodiment in which the condensation product is of alkylene oxides containing at least 20% propylene oxide and a polyhydric alcohol as defined more particularly in said claims and to the product of such a method; that affiant's

contribution to the subject matter of the said application pertained only to the preparation of cellular polyurethanes by a process wherein a catalyst containing a compound which in aqueous solution yields hydroxyl or substituted hydroxyl groups is used and that affiant did not contribute anything towards the preparation of polyurethanes from the condensation product of an alkylene oxide and a polyhydric alcohol as defined more particularly by Claims 35, 53, 54, 76 and 78 through 82; that an error was accidentally and inadvertently made at the time of filing the application in that an invention made jointly by affiant and Herbert L. Heiss and an invention to which affiant did not contribute were included in the one application Serial No. 373,036 and that the name of affiant should be deleted as a co-inventor of the subject matter of these claims; and that steps are being taken promptly after discovery of the mistake to delete the name of affiant from the application.

Further deponent sayeth not.

State of West Virginia }
County of Marshall } SS

James H. Saunders
James H. Saunders

Subscribed and sworn to before me this 12th day
of November, 1959.

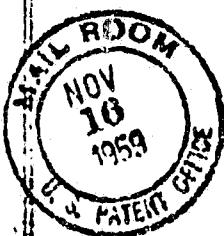
D. J. Smith, Jr., N.W.
Notary Public

My commission expires _____

My Commission Expires July 1, 1968

NOV 19 1959

DIVISION 50

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF

JAMES H. SAUNDERS ET AL.

SERIAL NO. 373,036

DIVISION 50

FILED: AUGUST 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAMEAFFIDAVIT OF HERBERT L. HEISS

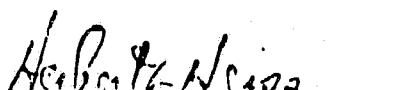
Herbert L. Heiss, being duly sworn, deposes and says that he is one of the joint applicants who filed patent application Serial No. 373,036 on August 7, 1953; that prior to the filing of the said application, affiant and his co-applicant James H. Saunders were engaged in a joint research program relating to the preparation of polyurethane plastics; that a large part of the research work conducted prior to the filing of the said application and relating to polyurethane plastics was done jointly with the co-applicant James H. Saunders; that he has read the Amendment filed September 15, 1959, in patent application Serial No. 373,036 and that he understands that upon the entry of this Amendment by the Patent Office the only claims remaining in the application will be Claims 35, 33, 54, 76 and 78 through 82; that affiant understands that these claims are directed to a method for making a polyurethane comprising reacting an organic polyisocyanate and a polyalkylene ether prepared by condensation of an alkylene oxide with a polyhydric alcohol including an embodiment in which the condensation product is of alkylene oxides containing at least 20% propylene oxide and a polyhydric alcohol as defined more particularly in said claims and to the product of such a method; that affiant alone conceived the idea of preparing a polyurethane

Oct 19 1959

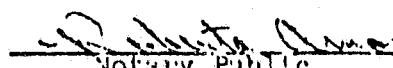
by such a process and that all work which resulted in that invention was done by him or under his direction and that James H. Saunders' contribution to the subject matter of the said application pertained only to the preparation of cellular polyurethanes by a process wherein a catalyst containing a compound which in aqueous solution yields hydroxyl or substituted hydroxyl groups is used and that James H. Saunders did not contribute anything towards the preparation of polyurethanes from the condensation product of an alkylene oxide and a polyhydric alcohol as defined more particularly by Claims 35, 53, 54, 76 and 78 through 82; that an error was accidentally and inadvertently made at the time of filing the application in that an invention of affiant alone and an invention made jointly by affiant and James H. Saunders were included in the one application Serial No. 373,036 and that the name of James H. Saunders should be deleted as a co-inventor of the subject matter of claims 35, 53, 54, 76 and 78 through 82; and that steps are being taken promptly after discovery of the mistake to delete the name of James H. Saunders from the application.

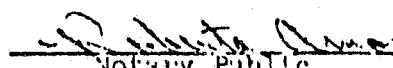
Further deponent sayeth not.

State of West Virginia }
 County of Marshall } SS


Herbert L. Neiss

Subscribed and sworn to before me this 12th day
 of November, 1959.


Notary Public
 My commission expires _____


My Commission Expires July 1, 1968

POLICE
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THE COMMERCIALS OF PATENTS
WASHINGTON 25, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting
this application should give the
serial number, date of filing,
and name of the applicant.

PAPER NO. 31

Cicelle W. Upchurch
1815 Washington Road.
Pittsburgh 34, Pa.

Please find below a communication from the
EXAMINER in charge of this application.

Robert C. Waters
Commissioner of Patents

Applicant:	Herbert L. Heiss
Ser. No.	323,036
Filed	AUGUST 7, 1953
For NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAME	

DLC 2 1954

16-93457-4 000

Responsive to letter of November 16, 1959.

The amendment, oath and affidavits of September
15, 1959 (Paper No. 27) and November 16, 1959 (Paper No. 30)
have been entered. Accordingly, the instant application has
been converted from joint to sole inventorship; the sole
inventor being Herbert L. Heiss.

JRC

D. E. Czajakow

O'Driscoll
Examiner

649a

AC-30
ATTY.
ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting
this application should give the
serial number, date of filing,
and name of the applicant.

PAPER NO. 32

Cleelle W. Upchurch
1815 Washington Road
Pittsburgh 34, Pa.

Please find below a communication from the
EXAMINER in charge of this application.

Robert Clinton
Commissioner of Patents.

Applicants	
Herbert L. Heiss	
Ser. No.	
373,036	
Filed	
August 2, 1959	
For	
NOVEL RESINOUS COMPO- SITIONS AND METHOD OF PRODUCING SAME	

DEC 23 1959
PATENT OFFICE
MAILED

10-3847-4 320

90414

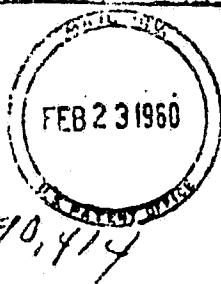
The letter and affidavits identifying this application as the sole invention of Herbert L. Heiss, formerly having status as a joint inventor in the case, have been entered.

Interference No. 90,414, Price v. Saunders and Heiss, involving the above identified application is hereby reformed, the party Saunders and Heiss being changed from Saunders and Heiss as joint inventors to Herbert L. Heiss as sole inventor.

The counts remain the same.

Arnold
Examiner

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No 218

FEB 26 1960
X 33

IN THE UNITED STATES PATENT OFFICE

DIVISION
APPLICATION OF
HERBERT L. HEISS
SERIAL NO. 373,036
FILED: August 7, 1953
TITLE: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

DIVISION 50

INTERFERENCE NO. 90,414

The Honorable Commissioner of Patents

Washington 25, D. C.

Sir:

Please address all future correspondence in the above
identified application to:

Clelle W. Upchurch
Penn-Lincoln Parkway West
Pittsburgh 5, Pennsylvania

Respectfully,

Clelle W. Upchurch
Clelle W. Upchurch
Attorney for Applicant

It is hereby certified that a copy of the foregoing is being mailed to
T. A. TeGrotenhuis, the attorney in charge of this interference in the
firm of McCoy, Greene & TeGrotenhuis, attorneys for Party Price on the

22nd day of February, 1960.

141

Clelle W. Upchurch
Clelle W. Upchurch, Attorney for Heiss

141



651a

No 218

31

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF

HERBERT L. HEISS

SERIAL NO. 373,036

FILED: AUGUST 7, 1953

TITLE: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

DIVISION 50

A M E N D M E N T

The Honorable Commissioner of Patents
Washington 25, D.C.

Sir:

Please add the following claims:

-- 83. A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) a hydroxy terminated polyether glycol polymer which is a condensation product of an alkylene oxide having from 2 to 3 carbon atoms and from about 7.5 to about 10 mol per cent based on the alkylene oxide of a polyhydric alcohol having less than 7 carbon atoms and having 3 to 4 primary hydroxyl groups, at least 20 per cent of said alkylene oxide having more than 2 carbon atoms, and (2) at least about 1 1/2 mols per mol of an organic diisocyanate based on said polyether glycol, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether glycol polymer is formed.

142

84. A process of preparing a polyurethane reaction product comprising the steps of mixing (1) a liquid hydroxyl terminated polyether glycol polymer which is a condensation product of an alkylene oxide of 2 to 3 carbon atoms inclusive, at least 20 per cent of said alkylene oxide having more than 2 carbon atoms and about 7.5 to about 10 mol per cent based on the alkylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 4 hydroxyl groups and (2) at least about 1.1 mols per mol of said condensation product of an organic polyisocyanate having 2 to 3 functional isocyanate groups, and reacting the mixture to form a reaction product having a chain length substantially greater than that of said polyether glycol polymer.

85. A product made according to process of Claim 83.

86. A product made according to process of Claim 84. --

REMARKS

The above claims are being added in conformance with the accompanying "Contingent Motion To Substitute 'Card and Card' Counts" and correspond to proposed Counts H(1) through H(4), respectively.

Respectfully submitted,
HERBERT L. HEISS

By Cicile W. Upchurch
Cicile W. Upchurch
Attorney for Applicant

Pittsburgh, Pennsylvania
April 29, 1960
CWU/cm



653a

KC

DOCKET L-101
FEB 21 1961

IN THE UNITED STATES PATENT OFFICE

IN RE APPLICATION OF

HERBERT L. HEISS

SERIAL NO. 373,036

FILED: August 7, 1953

Division 50

Interference No. 90,414

ENTITLED: NOVEL RESINOUS
COMPOSITIONS AND
METHOD OF PRODUCING
SAME

POWER OF ATTORNEY

Commissioner of Patents

Washington 25, D.C.

Sir:

Please recognize Fulton B. Flick, Registration No. 12,919, a member of the firm of Brown, Critchlow, Flick and Peckman, Room 1706 First National Bank Building, Pittsburgh 22, Pennsylvania, as Associate Attorney for me in the above identified application, and please continue to address all future communications to Clelio W. Upchurch, Penn Lincoln Parkway West, Pittsburgh 5, Pennsylvania.

Respectfully submitted,

Frederick K. Murdock

Frederick K. Murdock
Principal Attorney for
Herbert L. Heiss

St. Louis, Missouri
February 17, 1961
FWM:mlr

144

PROOF OF SERVICE

It is hereby certified that a copy of this "Power of Attorney" was this 17th day of February, 1961 forwarded by first class mail, postage prepaid, to Mr. T. H. TeGrotenhuis, a member of the firm of McCoy, Greene and TeGrotenhuis, Bulkley Building, Cleveland 15, Ohio, attorney of record for the Party Price.

Frederick M. Murdock
Frederick M. Murdock
Principal Attorney for
Herbert L. Weiss

655a

218-U

RECEIVED
JUN 16 1962
FIRST ASSISTANT COMMISSIONER

#36

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF: HERBERT L. HEISS
SERIAL NUMBER: 373,036
FILED: August 7, 1953
FOR: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

DIVISION 50
APPEAL NO. 24,205

PETITION FOR EXTENSION OF TIME
FOR FILING BRIEF ON APPEAL

Your Petitioner, Herbert L. Heiss, by means of his attorney, respectfully petitions the Honorable Commissioner of Patents to extend the time for filing a Brief in the matter of the above identified Appeal before the Board of Appeals for a period of sixty (60) days from the date the Brief is now due, July 21, 1962, until September 19, 1962.

In Paper No. 26 dated July 30, 1959, the Board of Appeals suspended proceedings until sixty days after termination of the Interference in which this Application had become involved. The Interference terminated on May 22, 1962.

Counsel for petitioner has discussed the claims remaining in the Application and the decision of the Board of Interference Examiners with the Examiner handling Ex parte matters. The Examiner is preparing to furnish a letter under Rule 266. It is agreed between the Examiner and Counsel that a proper brief cannot be filed until some issues arising from the Interference have been settled. The claims now under Appeal will require amendment because of the Interference but cannot be amended until the Examiner has furnished an action under Rule 266.

Extension of time
to SEP 1 " 1962
GRANTED

146

JUN 26 1962

Edward J. Reynolds
First Assistant Commissioner

146

The requested extension of time will be required for the Examiner to act upon the case and for counsel to place this application in condition for appeal in view of the Examiner's position following the Interference. In this way, it will be possible to write one Brief and cover all appealable matters at one time.

It is hereby certified that the foregoing request for additional time is made in good faith and not for the purposes of delay.

Respectfully submitted,

Cielle W. Upchurch
Cielle W. Upchurch
Attorney for Applicant

Pittsburgh, Pennsylvania
CWU:nms
June 18, 1962

POL-238

ADDRESS BELOW
THE COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

COPY MAILED
JUN 26 1962
COMMISSIONER'S OFFICE

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

437

June 26, 1962

Applicant: Herbert L. Heiss

Serial No. 373,036

Appeal No. 242-05

A request for extension of time for filing
a brief on appeal in the above identified application
has been filed.

The request has been granted by the First
Assistant Commissioner and the time is extended to
September 19, 1962.

By direction of the
First Assistant Commissioner

Charles E. Baber

Clella W. Upchurch
Penn-Lincoln Parkway West
Pittsburgh 5, Pa.

148

USCOMM-DC

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658a
U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting
this application should cite the
serial number, date of filing,
and name of the applicant.

PAPER No. 38

Cleelle W. Upchurch
Penn-Lincoln Parkway West
Pittsburgh 5, Pennsylvania

Please find below a communication from the
EXAMINER in charge of this application.

Commissioner of Patents.

Applicant:		Herbert L. Heiss
Ser. No.	373,036	
Filed	August 7, 1953	
For NOVEL RESINOUS COMPOSITIONS AND METHOD OF PRODUCING SAME		
		Aug 13 1962
		50

10-CAS-6 676

SHORTENED TIME FOR REPLY

Additional art cited.

Windemuth et al 2,948,691 Aug. 9, 1960 260/2.5A
(Filed May 6, 1952)

- 1) In view of the newly cited Windemuth et al patent, the finality of the rejection of October 2, 1958 is hereby withdrawn.
- 2) The amendment of February 6, 1959 (paper No. 18) which was submitted in response to the above referred to final Office action has not been entered notwithstanding the withdrawal of the finality of the above referred to rejection. This is so in view of entry of the subsequent supplemental amendment of September 15, 1959 (Paper No. 27) which directed the cancellation of all the claims except claims 35, 53, 54, 76, and 78 to 82.
- 3) Claims 83 to 86 which were presented in the amendment of May 2, 1960 (Paper No. 34) have not been entered since they were presented in a "Contingent Motion To Substitute 'Card and Card' Counts" in Interference No. 90,414 which was not granted; see the Decision on Motions dated August 15, 1960 (Paper No. 30) appearing in the above referred to Interference.

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4) Claims 35, 53, 54, 76 and 78 to 82 appear herein.

5) Claims 35 and 53 are rejected as fully met by Windemuth et al. Windemuth et al disclose a polyurethane which is the reaction product of an excess of an organic polyisocyanate and a triol which is the condensate of an alkylene oxide such as ethylene oxide and an organic trihydroxy compound such as trimethylolpropane.

6) Claims 76 and 78 to 80 are rejected as unpatentable over Windemuth et al.

Windemuth et al has been described above. Admittedly, this patent does not disclose a polyether having "at least 20 per cent of an alkylene oxide having more than 2 carbon atoms" as recited in claims 76 and 78 to 80. However, this limitation does not patentably define over Windemuth et al since it draws to new matter. There is no basis for this expression as such in the case.

7) Claim 54 is rejected as unpatentable over Windemuth et al in combination with Rinke et al.

Windemuth et al has been described above. Rinke et al disclose the reaction of a polyether glycol (ex. 4) with an excess of an organic diisocyanate in the presence of an organic liquid having a boiling point of at least about 200°C (column 1, line 53 and ex. 23). The substitution of the trihydroxy polyether of Windemuth et al for the dihydroxy polyether of Rinke et al or the use

Serial No. 373,036

-3-

of the Rinke et al organic liquid in Windemuth et al is considered to be obvious to one skilled in the art. This is so since each of the references is concerned with the preparation of polyurethanes from organic polyisocyanate/polyetherpolyol reaction products.

- 8) Claims 76 and 78-80 are rejected as containing new matter in the expressions "a molecular weight of at least 600". There is no basis for this expression in the case as originally filed. Note the Board of Interference Examiners' Decision dated March 23, 1962 in Interference No. 90,414 wherein applicant was denied the right to make claims containing the above molecular weight since there was no reasonable basis therefor in the case.
- 9) Claims 76 and 78-80 are rejected as containing new matter in "at least 20 percent ---more than 2 carbon atoms". There is no basis for this specific language in the case.
- 10) Claims 81 and 82 are allowable as at present advised.
- 11) A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE THREE MONTHS FROM THE DATE HEREOF.

APPROVED
FOR SHORTENED PERIOD

D. E. Czaja:car

AUG 10 1967
J. G. Stone
SUPERVISORY EXAMINER

R. J. Berenz
Acting Examiner

661a

MO 218-U



PAPER NO. 39/10
RECEIVED

SEP 27 1953

DIVISION 50 ✓

IN THE UNITED STATES PATENT OFFICE

In re the Application of

HERBERT L. HEISS

Serial No. 373,036

) DIVISION
50 ✓

Filed: August 7, 1953

Title: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

AMENDMENT

The Honorable Commissioner of Patents

Washington 25, D. C.

Sir:

In response to the Office Action dated August 13, 1962
please amend the application as follows:

Cancel Claims 35, 53, 54, 76 and 78 through 80 and

rewrite them as follows:

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Z 3. 87. The reaction product of (1) a condensate of propylene oxide and a polyhydric alcohol having from 3 to 4 hydroxyl groups, and (2) a member selected from the group consisting of an organic polyisocyanate and an organic polyisothiocyanate, the amount of (2) being in excess of that theoretically required to react with the reactive hydrogens of said condensate.

4. 88. A method for making a polyurethane reaction product which comprises mixing (1) a condensate of propylene oxide and a trihydric alcohol with (2) an organic polyisocyanate in a ratio of greater than one NCO_{H_2} per reactive hydrogen of said condensate, and reacting the mixture until a second polymer having a chain length greater than that of said condensate is formed.

5. 89. The product of Claim 87 wherein the said group member is an organic polyisocyanate.

5. 90. A process for making a reaction product which comprises reacting (1) a condensate of propylene oxide and a polyhydric alcohol having from 3 to 4 hydroxyl groups and (2) a member selected from the group consisting of an organic polyisocyanate and an organic polyisothiocyanate, the amount of (2) being in excess of that theoretically required to react with the reactive hydrogens of said condensate.

6
91. The process of ⁵Claim 90 wherein the said condensate is reacted with an organic polyisocyanate.

7
92. A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) an hydroxy terminated polyether polymer which is a condensation product of propylene oxide and a polyhydric alcohol having less than 7 carbon atoms and having 3 to 4 primary hydroxyl groups, and (2) an organic diisocyanate, in an amount providing a ratio of NCO groups to the reactive hydrogens of said polyether greater than 1 to 1, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether polymer is formed.

8
93. A process of preparing a polyurethane reaction product comprising the steps of mixing (1) a liquid hydroxyl terminated polyether polymer which is a condensation product of propylene oxide and an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 4 hydroxyl groups, and (2) an organic polyisocyanate having 2 to 3 functional isocyanate groups in a ratio of greater than one NCO per reactive hydrogen of said polyether polymer, and reacting the mixture to form a reaction product having a chain length substantially greater than that of said polyether polymer.

94. A product made according to the process of

Claim 92.

95. A product made according to the process of

Claim 93.

10 96. A process of forming a polyurethane

comprising the steps of mixing (1) a condensation product of propylene oxide and glycerine, and (2) an organic polyisocyanate in a ratio of greater than one -NCO per reactive hydrogen of said condensation product, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

11 97. A process of forming a polyurethane reaction

product comprising the steps of mixing (1) a condensation product of propylene oxide and an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 4 hydroxyl groups and (2) an organic diisocyanate in a ratio providing more than one -NCO per reactive hydrogen of said condensation product, and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

1298. A process of forming a polyurethane reaction product comprising the steps of mixing a first polymer comprising a condensation product of propylene oxide and an aliphatic polyhydric alcohol of less than 7 carbon atoms and having 3 to 4 hydroxyl groups, and at least about 2 mols, based on the amount of said condensation product, of an organic diisocyanate and reacting the mixture until a second polymer having a chain length substantially greater than the first polymer is formed.

REMARKS

Reconsideration of the application in view of the foregoing amendment and the following explanation is respectfully requested. The recent interview with the Examiner is acknowledged with appreciation.

All of the claims, except for allowed Claims 81 and 82 have been cancelled and rewritten as Claims 87 through 98. It is submitted that the new set of claims cannot be properly rejected as unpatentable over Windemuth et al. All of the claims require that the alkylene oxide be propylene oxide. Windemuth et al. discloses only ethylene oxide. Since Windemuth et al. does not disclose the polyether covered by the new set of claims, Applicant is not merely

substituting the Windemuth et al. polyether for the one disclosed by Rinke et al. It is submitted that no one reading the two patents together could conclude that one must use a polyoxypropylene ether instead of the polyethylene ether glycol of Windemuth et al. in order to make a polyurethane of improved characteristics.

The new claims do not include the limitation objected to in Paragraph 9 of the Office Action.

Of the newly presented set of claims, Claim 87 is similar to former Claim 35, and is directed to the reaction product obtained when an organic polyisocyanate or organic polyisothiocyanate is reacted with a propylene oxide-polyhydric alcohol condensate.

Claim 88 specifies that the polyhydric alcohol is to be a trihydric alcohol and is similar to cancelled Claim 53.

Claim 89 is dependent upon Claim 87, but specifies that an organic polyisocyanate is used.

Claim 90 is a process claim directed to the preparation of a polyurethane from a propylene oxide-polyhydric alcohol condensate and a polyisocyanate or polyisothiocyanate.

Claim 91 is specific to an organic polyisocyanate.

Claim 92 corresponds to cancelled Claim 76, but is directed to the preparation of a polyurethane using a propylene oxide-polyhydric alcohol condensate.

Claim 93 is similar to former Claim 78 and distinguishes from the other claims by specifying a liquid polyether is reacted with a polyisocyanate.

Claims 94 and 95 correspond to former Claims 79 and 80 and are directed to the products of Claims 92 and 93, respectively.

Claim 96 is directed to the preparation of a polyurethane by a process in which a condensate of propylene oxide and glycerine is used. This claim differs from the other claims in this respect.

Claim 97 is similar in some respects to Claim 82 but differs therefrom in the ratio of diisocyanate to polyether.

Claim 98 requires at least two mols of diisocyanate per mol of condensation product.

It is submitted that the claims as now written are allowable, so early allowance is earnestly solicited.

Respectfully submitted,

HERBERT L. HEISS

By Cleile W. Upchurch

Cleile W. Upchurch
Attorney for Applicant

Pittsburgh, Pennsylvania
September 17, 1962
CWU:nms

U.S. GOVERNMENT
THE DEPARTMENT OF COMMERCE
WASHINGTON, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

In communications respecting
this application should give the
serial number, date of filing,
and name of the applicant.

PAPER No. 40

Cicelle W. Upchurch
Penn-Lincoln Parkway West
Pittsburgh 5, Pa.

Please find below a communication from the
EXAMINER in charge of this application.

Commissioner of Patents.

Applicant:	Herbert L. Heiss
Ser. No.	373,036
Filed	Aug. 7, 1953
For	NOVEL RESINOUS COM- POSITIONS AND METHOD OF PRODUCING SAME

MILED

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RECORDED

RECORDED

- 1) Claims 81, 82 and 87 to 98 appear herein.
- 2) Claims 81, 82, 88, 90 to 93 and 96 to 98 are allowed.
- 3) Claims 87, 89, 94 to 95 are rejected as being unduly multiplied.

These claims are product-by-process claims. As a general rule, applicant is entitled to only one such claim unless there are material differences between the products produced by the processes recited in the different claims; section 706.03 (E) M.P.E.P. (3rd Ed.). The claims, as presently worded, do not contain the necessary material differences. For example, the only difference between claims 87 and 89 (89 being dependent upon 87) is that claim 89 is limited to an organic polyisocyanate. This is not a material difference since the organic polyisocyanate is already specifically included in claim 87 as one of the members of the Markush group of components which can be reacted with the condensate. Likewise, there is no material difference between the products of claims 94 and 95. Claims 94 and 95

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Serial No. 373,036

-2-

depend from process claims 92 and 93. The processes recited in claims 92 and 93 are the same. The only differences are in (1) The definition of the isocyanate component; viz. claim 92: "organic diisocyanate" and claim 93: "an organic polyisocyanate having 2 to 3 functional isocyanate groups" and (2) the manner of expressing the amount of the isocyanate component; each claim, in essence, requiring that an excess be present. These differences are not of such a degree that they would result in such differences that would entitle applicant to both claims 94 and 95. Finally, the products of claims 94 and 95 are encompassed by the products recited in claims 87 and 89.

- 4) This rejection is made FINAL.

L.J. Beccozzi
Acting Examiner

DL
DECzaja/bmh



PAPER NO. 117
RECEIVED

NOV 8 1962

DIVISION 50

IN THE UNITED STATES PATENT OFFICE

In the Application of

HERBERT L. HEISS

Serial Number: 373,036

) DIVISION
50

Filed: August 7, 1953

Title: NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

AMENDMENT AFTER FINAL REJECTION

The Honorable Commissioner of Patents

Washington 25, D. C.

Sir:

In response to the Office Action dated October 12, 1962,
please amend the application as follows:

Claim 87, line 3, cancel "a member selected from the group
consisting of"; line 4, cancel "and an organic polyisothiocyanate,";
same line, after "polyisocyanate" insert a comma --(,)--.

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Cancel Claims 89 and 94.

Claim 93, line 4, cancel "an aliphatic" and before "polyhydric".

insert -- a --.

REMARKS

Reconsideration of the application in view of the foregoing amendments is respectfully requested. As pointed out at the recent interview, which is acknowledged with appreciation, section 706.03 (E) MPEP (3rd Edition) does not prohibit the allowance of more than one product-by-process claim. It is understood that both claims will be allowed.

The above amendment removes the last issue involved in this application, so it is submitted that the case is now in condition for allowance. Early allowance, therefore, is earnestly solicited.

Respectfully submitted,

HERBERT L. HEISS

By Clella W. Upchurch

Clella W. Upchurch
Attorney for Applicant

Pittsburgh, Pennsylvania
5 November 1962
CWU:nms

672a

A 2901

Paper No.: 42
Serial No.: 373,036

REFERENCES CITED

The following references are of record in the patented file of this patent:

UNITED STATES PATENTS

Name	Number	Date
Pratt	2,349,756	May 23, 1944
Rinke et al.	2,511,544	June 13, 1950
Simon et al	2,577,281	Dec. 4, 1951
Schmidt et al	2,621,166	Dec. 9, 1952
Seeger	2,625,531	Jan. 13, 1953
Seeger	2,625,532	Jan. 13, 1953
Mastin et al	2,625,535	Jan. 13, 1953
Windemuth	2,650,212	Aug. 25, 1953
Simon et al	2,772,245	Nov. 27, 1956
Reis	2,779,689	Jan. 29, 1957
Detrick et al	2,787,601	Apr. 2, 1957
Windemuth	2,948,691	Aug. 9, 1960

FOREIGN PATENTS

Country	Number	Date
France	869,243	Sep. 29, 1942
France	875,643	Sep. 29, 1942
France	890,915	Feb. 22, 1944
France	897,067	Mar. 12, 1945

OTHER REFERENCES

- Q DeBell; "German Plastics Practice", 1946, page 302.
- Q "Chemical Engineering", Volume 57, No. 4, April, 1950,
pages 165 and 166.

673a

POL-85a
8-26-58

ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting
this application should give the
serial number, date of filing,
and name of the applicant.

NOTICE OF ALLOWANCE

The application for patent identified below has been examined and found allowable
for issuance of Letters Patent.

	FILING DATE	SERIAL NO.	NO. OF CLAIMS ALLOWED	EXAMINER	DIV.
APPLICANT	08/07/53	373036	12	L. J. Borcovitz	SC
ASSIGNEE	He'son, Herbert L., Anniston, Ala.			MAILED DEC. 13, 1953	
TITLE OF INVENTION	Polyurethane reaction product and method for making same AS MENTIONED BY EXAMINER			CLASS-SUB	260/077.5

With the allowance of the application the final fee becomes due. This fee is thirty dollars (\$30) plus one dollar (\$1) for each claim allowed in excess of twenty (20) and must be paid within 6 months from the date of this notice. Failure to remit the final fee will result in the patent being withheld from issue.

As a convenience in remitting this fee, use of the enclosed Form POL-85a is suggested. The final fee will not be received from anyone other than the applicant, his assignee or attorney, or a party in interest as shown by the records of the Patent Office. If no entry appears in the space labeled "assignee," above, a form is enclosed relating to the address of the inventor(s) which requires your attention.

If it is desired to have the patent issued to an assignee or assignees, an assignment, together with the fee for recording the same, must be filed in this Office on or before the date of payment of the final fee.

The patent will be issued and forwarded within approximately two months after receipt of the final fee.

By direction of the Commissioner.

Clellie W. Upchurch
Penn-Lincoln Parkway West
Pittsburgh 5, Pa.

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Mo 218-U

PAPER NO. _____
RECEIVED

JAN 10 1963

DIVISION 58

IN THE UNITED STATES PATENT OFFICE

APPLICATION OF

HERBERT L. HEISS

SERIAL NO. 373,036

FILED: August 7, 1953

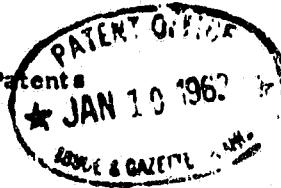
**TITLE: POLYURETHANE REACTION PRODUCT
AND METHOD FOR MAKING SAME**

Patent #47

DIVISION 50

The Honorable Commissioner of Patents

Washington 25, D. C.



Sir:

Please place the enclosed Supplementary Oath in the file
of the above-identified patent application.

Respectfully submitted,

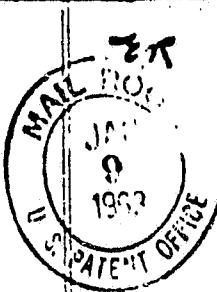
HERBERT L. HEISS

By Clellie W. Upchurch
Clellie W. Upchurch
Attorney for Applicant

Pittsburgh, Pennsylvania
/jcp
January 8, 1963

MO 218-U

675a



PAPER NO. REC'D
JAN 10 1963

IN THE UNITED STATES PATENT OFFICE DIVISION 54

APPLICATION OF:

HERBERT L. HEISS

SERIAL NO. 373,036

FILED: AUGUST 7, 1953

TITLE: POLYURETHANE REACTION PRODUCT
AND METHOD FOR MAKING SAME

STATE OF WEST VIRGINIA

COUNTY OF MARSHALL

DIVISION 50

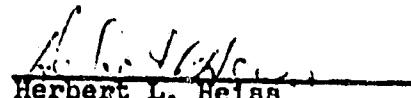


SUPPLEMENTARY OATH

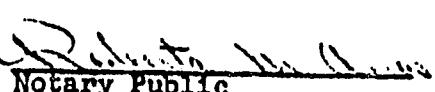
Being duly sworn, I Herbert L. Heiss depose and say that I am a citizen of the United States, residing at Route 1, Cider Run, New Martinsville, West Virginia; that I have read the specification of the above-identified application and the amendments filed March 24, 1959, September 26, 1962 and November 6, 1962 and that I verily believe myself to be the original, first and sole inventor of the subject matter of all the allowed claims; that the subject matter of the aforementioned amendments and the allowed claims is part of my invention and was invented before the filing of the above-identified application; that I do not know and do not believe that this invention was ever known or used before my invention thereof, or patented or described in any printed publication in any country before my invention thereof, or more than one year prior to the filing date of this application, or in public use or on sale in the United States more than one year prior to the filing date of this application; that this invention has not been patented in any country foreign

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to the United States on an application filed by me or my legal representatives or assigns more than twelve months prior to the date of this application; and that applications for patents on the invention were not filed in any country foreign to the United States prior to the filing date of this application in the United States; and that the invention as claimed in all of the allowed claims has not been abandoned.


Herbert L. Heiss

On this 3rd day of January, 1963, before me personally appeared Herbert L. Heiss to me personally known, and known to me to be the person who signed the foregoing, and acknowledged the signing of same as his free act and deed.


Notary Public

My Commission Expires July 1, 1968
My commission expires

677a

POL-58A
6-26-58U. S. Department of Commerce
Patent Office

Mr. 218-11

FINAL FEE TRANSMITTAL

This form is provided for convenience in transmitting final fees to the Patent Office. When properly completed it may be used in lieu of a formal transmittal letter. Respondents will note and fill in items numbered 1 thru 6 below. The Final Fee Receipt, in all cases, will be mailed to the address appearing in box at lower left of this form. If desired, use the reverse side of your Notice of Allowance for carbon copy when completing this form.

1. The COMMISSIONER OF PATENTS is requested to apply the accompanying fee to the case identified below, and deliver the patent as indicated.

June 5, 1963
Date6
1963
U.S. PATENT OFFICEClell W. Zuckerman
Attorney, Agent or Applicant

NOTE—Final fees will not be received from other than the applicant, his assignee, or attorney, or a party in interest as shown by the records of the Patent Office. Final fees will not be applied to pending applications.

	FILING DATE 08/07/53	SERIAL NO. 273036	NO. OF CLAIMS ALLOWED 12	EXAMINER L. J. Bercovits	DIV. 50
APPLICANT	Heiss, Herbert L., Anniston, Ala.				MAILED DEC. 11, 1962
ASSIGNEE					NOTICE OF ALLOWANCE DATE CLASS SUB 260/077.5
TITLE OF INVENTION AS AMENDED BY EXAMINER	Polyurethane reaction product and method for making same				3. FEE ENCLOSED \$ 30.00
2. DEFERMENT: (Indicate below if desired)					
Please defer issuance of the patent for Three Months DEFERRED					
4. Assignee: (If assigned and name does not agree with corresponding space above) SEP 3 - 1963					
Mobilay Chemical Company and Monsanto Chemical Company Penn Lincoln Parkway West 800 North Lindbergh Boulevard Pittsburgh 5, Pennsylvania St. Louis 66, Missouri					
5. MAILING INSTRUCTIONS					

Note—The office will send the patent to the address entered in stub at left below unless you direct otherwise. Use the spaces provided to indicate any changes which affect the delivery of the patent.

5. Do not send the patent to the addressee listed below. Send patent to (check one)

Pattee
 Assignee

Associate Attorney (See specific authorization in file)
 Change of address—Attorney

The address of the person checked above is typed in Item 6 below.

6.

168

678a

	Filing Date 08/07/53	Serial No. 3730761	Fee \$30	Issue Date 09/03/63
INVENTOR	Heiss, Herbert L., Anniston, Ala.			
ASSIGNEE	1/2, Monsanto Chemical Company, and 1/2, Moway Chemical Company, means			
INVENTION	Polyurethane reaction product and method for making same			
POL-39 Modifications Requesting Deferred	Issue of the above identified allowed application for patent has been deferred as requested. 260/077.5.			
		Clellie W. Upchurch Penn-Lincoln Parkway West Pittsburgh 5, Pa.		Patent Office
U. S. Department of Commerce				

16.9

AO Form 120 (Rev. Oct. 1964)

In Re Patents

United States District Court

for the

Northern District of Illinois (CHICAGO)
Eastern DivisionCommissioner of Patents,
Washington 25, D. C.
Sm:

(Chicago) JUN 20 1968

In compliance with the Act of July 19, 1952 (66 Stat. 814; 35 USC 290), you are advised that there was filed on the 25th day of January, 1968, in this court an action, No. 68 C 150, entitled:

Name Jefferson Chemical Co.

Plaintiff,

Address Houston, Texas

versus

Name General Tire & Rubber Co.

Defendant,

Address Chicago, Illinois

brought upon the following patents:

PATENT NO.	DATE OF PATENT	PATENTEE
1. 3,102,875	Sept. 3, 1963	Plaintiff
2.		
3.		
4.		
5.		

In the above-entitled case, on the _____ day of _____, 19____, the following patents have been included by _____ (insert amendment, answer, cross bill, or other pleading):

PATENT NO.	DATE OF PATENT	PATENTEE
1.		
2.		
3.		
4.		
5.		

In the above-entitled case the following decision has been rendered or judgment issued:

Albert A. Wagner, Jr.

Clerk.

By Beverly V. Peters
Deputy Clerk.

Date January 25, 1968

In Re Patents

United States District Court
for the

SOUTHERN DISTRICT OF NEW YORK

Commissioner of PATENTS,
Washington 25, D. C.

Sir:

In compliance with the Act of July 16, 1952 (66 Stat. 814; 35 USC 290), you are advised that there was filed on the 26th day of MARCH, 1968, in this court an action, No. 68Civ.1227, entitled:

Name THE GENERAL TYRE & RUBBER COMPANY Plaintiff,

Address 1708 Englewood Ave., Akron, Ohio

versus

Name JEFFERSON CHEMICAL COMPANY, INC., Defendant,

Address 200 Madison Ave., NYC, N.Y.,

brought upon the following patents:

PATENT NO.	DATE OF PATENT	PATENTEE
3,292,875	9-1-63	DEITA

In the above-entitled case, on the _____ day of _____, 19____, the following patents have been included by _____ (insert amendment, answer, cross bill, or other pleading):

PATENT NO.	DATE OF PATENT	PATENTEE

In the above-entitled case the following decision has been rendered or judgment issued:

JOHN J. OLEARY, JR.,

Clerk.

By *J. J. O'Leary* Deputy Clerk.Date 3-27-68

AO Form 120 (Rev. Oct. 1954)

In Re Patents

6-21

United States District Court

for the

Northern District of Illinois
Eastern DivisionCommissioner of PATENTS,
Washington 25, D. C.
Date:

SOLICITOR

JUN 18 1968

U. S. PATENT OFFICE

Chicago #46

In compliance with the Act of July 18, 1952 (46 Stat. 814; 35 USC 280), you are advised that there was filed on the 25th day of January 1968, in this court an action, No. 68 C 150, entitled:

Name Jefferson Chemical Co., Plaintiff,

Address Houston, Texas

versus

Name General Tire & Rubber Co., Defendant,

Address Chicago, Illinois

brought upon the following patents:

PATENT NO.	DATE OF PATENT	PATENTEE
1. 3,102,875	Sept. 3, 1963	Plaintiff
2.		
3.		
4.		

In the above-entitled case, on the _____ day of _____, 19____, the following patents have been included by _____ (insert amendment, answer, cross bill, or other pleading):

PATENT NO.	DATE OF PATENT	PATENTEE
1.		
2.		
3.		
4.		

In the above-entitled case the following decision has been rendered or judgment issued:

6-12-68 - Enter Summary Agreed Order dismissing complaint for lack of venue- AUSTIN, J.

Albert A. Wagner, Jr.
Clerk.

By Beverly Peters
Deputy Clerk.

Date June 13, 1968.

682a

SEARCHED

Class	Sub	Date	Ex'r
260	77.5A	4-5-54	OPM
260	2.5A	94-58	SEC
	77.5A		
260	2.5A	7'57	SEC
	77.5A		
260	above	8/58	SEC

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Refused	Rejected
Accepted	Allowed
(Through numbers)	Canceled
Revised	Deemed
No response	Dismissed
Received	Entered
Entered	Entered
Appealed	Appeal

CONTENTS

Archaeological papers.

SECTION

EXHIBITION APR 8 - 1954

10. The following table gives the number of hours worked by each of the 1000 workers.

RECEIVED FEB 27 1956
U.S. GOVERNMENT PRINTING OFFICE: 1956 1-244-24
U.S. GOVERNMENT ACCEPTANCE & LETTER FEB 27 1956

DEC 25 1956

JUL 31 1952

1948

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1970-31-2 New 16 1969

26. Letter by Bd -- Jul 30 1959
27. Letter -- Oct 17 1959
28. LETTER -- OCT 14 1959
29. LETTER -- OCT 20 1959
30. Letter -- Oct 26 1959
31. Letter -- DEC 1 1959
32. Letter (10914) -- DEC 23 1959
33. (See above) -- Oct 26 1959
34. (See above) -- Oct 26 1959
35. (See above) -- Oct 26 1959
36. (See above) -- Oct 26 1959
37. COMMISSION'S DECISION JUN 26 1961
RENTENED TIME FOR REPLY AUG 13 1961
38.
39. FINAL DECISION
40. -- OCT 12 1962
41. References
42.
43. Supplemental Oath JUN 9 1962
44. Notice of Suit
45. Notice of Suit MAR 26 1962
46. Notice of Suit JUN 13 1962
47.
48.
49.
50.

PLAINTIFF'S EXHIBITS 4A - L

Charts

Pages 684a to 695a



CARBON TETRAVALENT



OXYGEN DIVALENT



HYDROGEN MONOVALENT



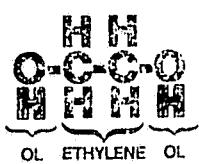
HYDROXYL GROUP (OL)
ONE ACTIVE HYDROGEN



WATER
TWO ACTIVE HYDROGENS



ALCOHOL, ETHYL ALCOHOL
ONE ACTIVE HYDROGEN
MONOFUNCTIONAL



GLYCOL ETHYLENE GLYCOL
TWO ACTIVE HYDROGENS
DIFUNCTIONAL

HO-**C**-C-OH MINUS H₂O

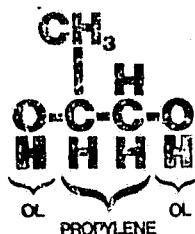
YIELDS



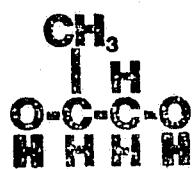
ETHYLENE OXIDE



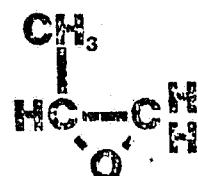
**PROPYL ALCOHOL
ONE ACTIVE HYDROGEN
MONOFUNCTIONAL**



**PROPYLENE GLYCOL
TWO ACTIVE HYDROGENS
DIFUNCTIONAL**

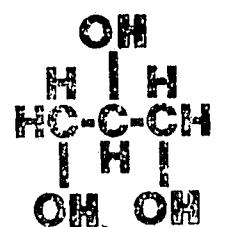


**PROPYLENE GLYCOL
MINUS H₂O**

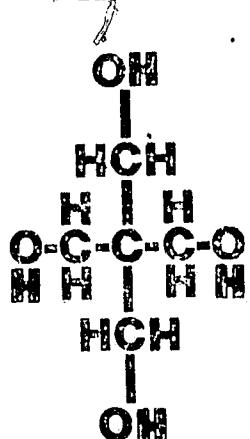


PROPYLENE OXIDE

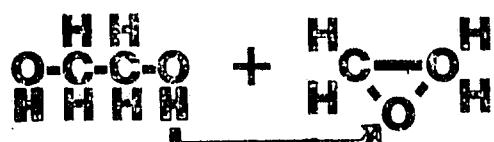
686a



GLYCEROL
THREE ACTIVE HYDROGENS
TRIFUNCTIONAL



PENTAERYTHRITOL
FOUR ACTIVE HYDROGENS
TETRAFUNCTIONAL



ETHYLENE GLYCOL + ONE ETHYLENE OXIDE

YIELDS



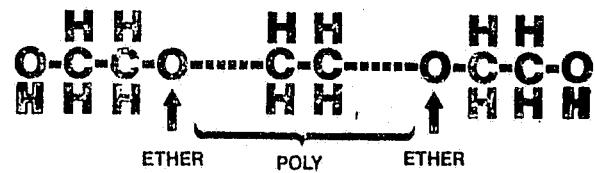
ETHER BOND

DI-ETHYLENE GLYCOL

DIFUNCTIONAL

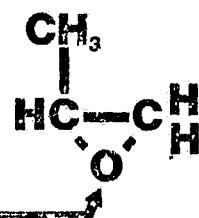
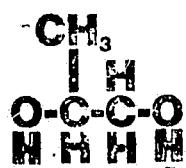
ETHYLENE GLYCOL + MANY (POLY) ETHYLENE OXIDES

YIELDS

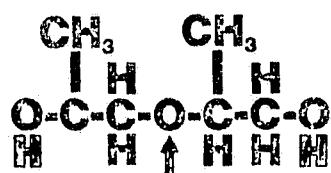


POLY-ETHYLENE-OXIDE

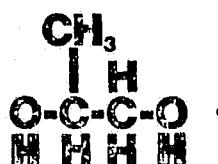
LINEAR POLYETHER
A POLYETHERPOLYOL
DIFUNCTIONAL



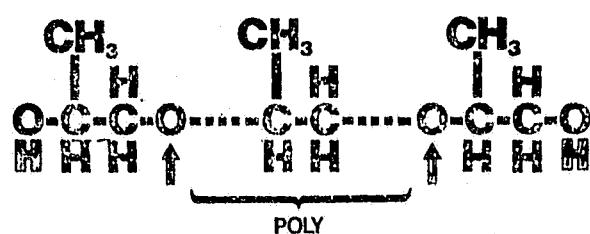
PROPYLENE GLYCOL + ONE PROPYLENE OXIDE
YIELDS



ETHER BOND
DI-PROPYLENE GLYCOL
DIFUNCTIONAL



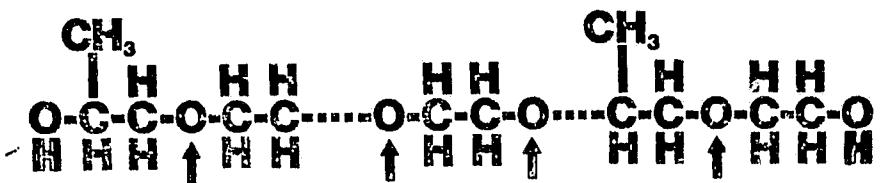
+ MANY(POLY) PROPYLENE OXIDES



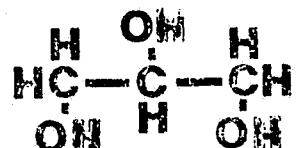
POLY-PROPYLENE-OXIDE

LINEAR POLYETHER
A POLYETHERPOLYOL
DIFUNCTIONAL

ETHYLENE GLYCOL + A MIXTURE OF MANY ETHYLENE
OXIDES AND PROPYLENE OXIDES
YIELDS



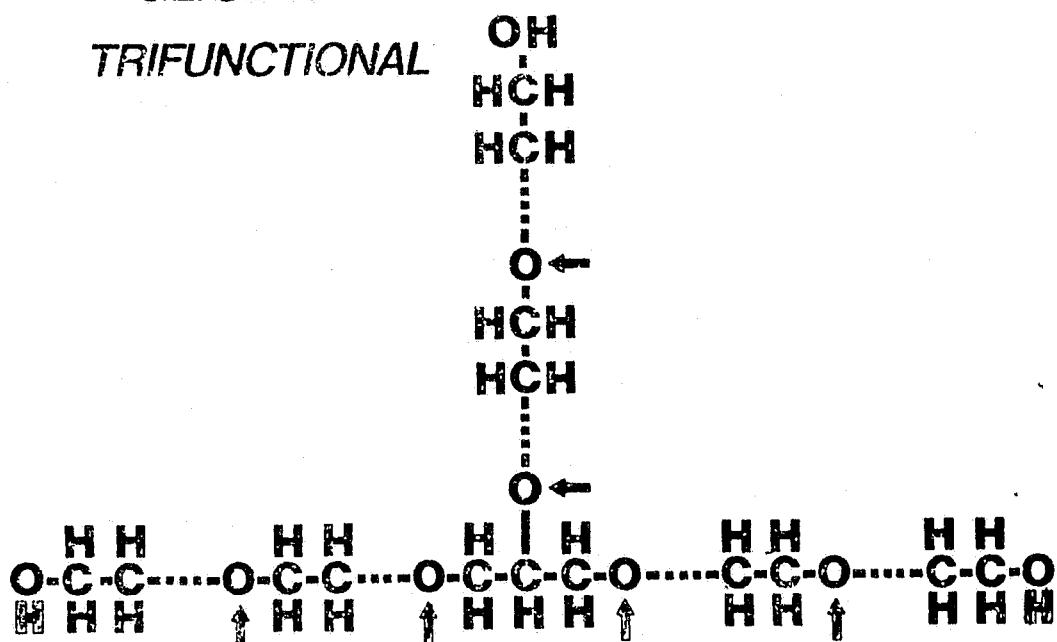
LINEAR COPOLYMER OF ETHYLENE-AND PROPYLENE OXIDE
DIFUNCTIONAL



690a

+ MANY ETHYLENE OXIDES
YIELDS

G
GLYCEROL
TRIFUNCTIONAL

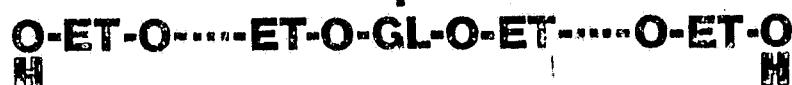


BRANCHED POLYETHYLENE OXIDE

TRIFUNCTIONAL

ETHYLENE
RESIDUE $\text{C}_2\text{H}_4 = \text{ET}$

GLYCEROL
RESIDUE $\text{C}_3\text{H}_5 = \text{GL}$



BRANCHED POLYETHYLENE OXIDE
A POLYETHERPOLYOL
TRIFUNCTIONAL

691a

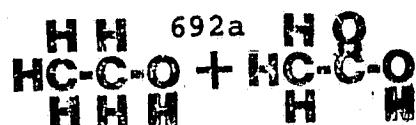
GLYCEROL + MANY PROPYLENE OXIDES
YIELDS

Pr = C_3H_6
PROPYLENE
RESIDUE



BRANCHED POLYPROPYLENE OXIDE

A POLYETHERPOLYOL
TRIFUNCTIONAL



ALCOHOL

ACETIC ACID

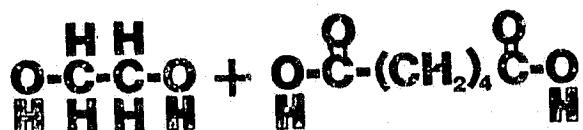
MONOFUNCTIONAL

MONOFUNCTIONAL

YIELDS



ETHYL ACETATE



ETHYLENE GLYCOL (ET)

ADIPIC ACID (AD)

DIFUNCTIONAL

DIFUNCTIONAL

YIELDS



LINEAR POLYESTER WITH TWO ACTIVE HYDROGENS

POLYESTERPOLYOL.

DIFUNCTIONAL

FORMATION OF A URETHANE LINKAGE (U)



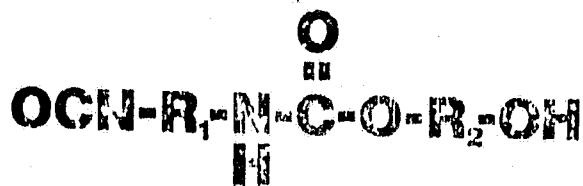
45
ISOCYANATE HYDROXYL



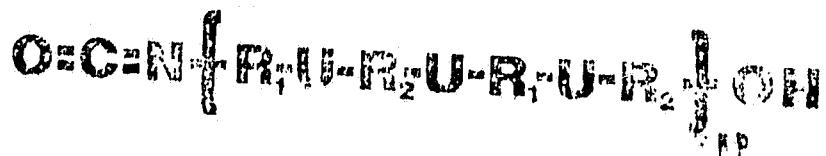
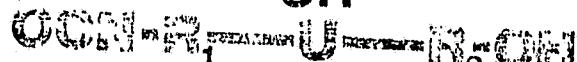
URETHANE LINKAGE

(U)

IN A DIOL (POLYESTER OR POLYETHER) IS REACTED WITH A DIISOCYANATE, A LINEAR POLYMER IS PRODUCED.



OR



POLYURETHANE

4 K

FORMATION OF CROSS-LINKED POLYURETHANE CHAINS FROM TRIFUNCTIONAL POLYOOLS



DIISOCYANATE



TRIHYDROXY
COMPOUND
TRIOL



POLYURETHANE NETWORK

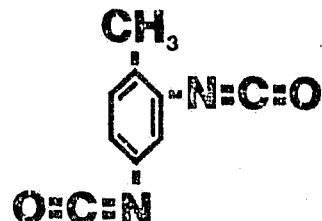
AND R_3 MAY BE ANY ORGANIC RESIDUE IN THE BACKBONE
OF THE DIISOCYANATE AND THE TRIOL.

695a



MDI

DIPHENYL METHANE DIISOCYANATE



TDI

TOLYLENE DIISOCYANATE



DIHYDROXY DIETHYL PHENYLENE ETHER

PLAINTIFF'S EXHIBIT 5

U. S. Patent No. 2,948,691, Erwin Windemuth, et al.

Pages 696a to 701a

United States Patent Office

2,948,691

Patented Aug. 9, 1960

1

2,948,691

HIGH MOLECULAR WEIGHT POLYETHER
URETHANE POLYMERS

Erwin Windemuth, Hermann Schnell, and Otto Bayer,
Leverkusen, Germany, assignors, by direct and mesne
assignments, of one-half to Mobay Chemical Com-
pany, St. Louis, Mo., a corporation of Delaware; and
one-half to Farbenfabriken Bayer Aktiengesellschaft,
Leverkusen Bayerwerk, Germany, a corporation of
Germany

No Drawing. Filed May 6, 1952, Ser. No. 286,425

Claims priority, application Germany May 10, 1951

28 Claims. (Cl. 260—2.5)

The present invention relates to high molecular weight polymers and to a process of producing same.

It is known in the art to produce polyglycolethers having one or more terminal hydroxyl groups by polymerizing alkylene oxides, for instance ethylene oxide, or by chemical addition of alkylene oxides to mono- or polyfunctional alcohols such as stearyl alcohol, ethylene glycol, trimethylolpropane, pentaerythrite etc. These polyglycolethers are generally soluble in water and organic solvents, except in aliphatic and cycloaliphatic hydrocarbons such as gasoline and cyclohexane. The molecular weight of these products varies depending on their mode of preparation.

In accordance with the present invention we have found that polyglycolethers of a molecular weight of at least 500, which have at least two terminal hydroxyl groups can be reacted with mono- or polyfunctional aliphatic or aromatic isocyanates. The reaction results in novel products which may be used for producing plasticizers, lubricants, plastics, spongy materials, gel formers, thickening agents, auxiliaries in textile industry, and the like.

In the above reaction polymers or addition products of alkylene oxides may be used as polyglycolethers. Examples of isocyanates are the aliphatic and aromatic monoisocyanates such as chlorohexyl isocyanate, phenyl isocyanate, and the appropriate polyfunctional isocyanates such for example as hexamethylene diisocyanate, naphthalene-1,5-diisocyanate, toluylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,4-phenylene diisocyanate, and 4,4'-diphenyldiisocyanate. Depending on the polyglycoether and the nature and quantity of the isocyanate used in the reaction, products are obtained which, as compared with the starting material, show modified properties and open new fields of application.

Thus, for instance, the reaction of polyglycolethers and aromatic or aliphatic monoisocyanates—depending on the molecular weight of the polyglycoether and the nature and quantity of the isocyanate—gives rise to products which are either insoluble in water, however, soluble in organic solvents or which dissolve in cold water but not in hot water. The products may be used as plasticizers and lubricants, furthermore as emulsifiers if long-chain aliphatic isocyanates, for instance, stearyl isocyanate, were used for their manufacture. In some cases, especially when working with aromatic isocyanates, chemical addition of the isocyanates to the hydroxyl groups occurs with selfheating on contacting the components. It is possible in all cases to convert all the hydroxyl groups into urethane groups at higher tempera-

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tures; if volatile isocyanates are present the reaction may be carried out by application of pressure.

By reacting polyglycolethers containing two hydroxyl groups in the molecule and polyfunctional, for instance bifunctional, isocyanates, products are obtained with an increase in molecular weight, which are of resinous character or thermoplastic. Products of this type dissolve in organic solvents, except in aliphatic hydrocarbons. Products produced in the reaction of polyglycolethers of a relatively low molecular weight and diisocyanates are generally insoluble in water but soluble in organic solvents. Products derived from polyglycolethers of high molecular weight, however, dissolve in water and organic solvents. Due to their compatibility with many natural or synthetic polymeric substances and their non-volatility the products may advantageously be used as addition for lacquers and plastics.

The reaction of polyglycolethers having three or more terminal hydroxyl groups with equivalent amounts of polyfunctional isocyanates results in cross-linked insoluble plastics. The properties of these plastics substantially depend on the starting materials used for their preparation. As a rule, hard products are obtained at room temperature when the starting materials have a high degree of cross-linkage whereas products of rubber elastic properties are obtained when the starting materials have a low degree of cross-linkage. Hard products are preferably prepared from polyglycolethers of a low molecular weight, say about 500 to 1000, whereas polyglycolethers of a high molecular weight, say about 3000-15000, are employed for preparing elastomers. The plastics are of interest because of their swelling properties. For instance, it is possible according to the invention to prepare rubber elastic products which are completely indifferent in aliphatic hydrocarbons, however, swell in contact with water.

When using polyfunctional isocyanates in quantities smaller than the equivalent ones a partial increase only in molecular weight occurs. The isocyanate modified polyglycolethers thus obtained still contain free hydroxyl groups. Depending on the quantity of the polyisocyanate added, it is possible to prepare in this way, like in the reaction of bi-functional polyglycolethers, products which dissolve in water and organic solvents, or which are soluble in organic solvents but insoluble in water. Another possibility of variation consists in the supplementary use of aliphatic or aromatic monoisocyanates which are reacted with the residual hydroxyl groups. In the reverse order, the polyglycolethers can partially be reacted first with monoisocyanates and, thereafter, follows the reaction of the rest of the hydroxyl group with polyfunctional isocyanates. The soluble representatives of this class of compounds may be used for a great number of applications. They are suitable for instance as thickening agents, assistants in textile industry, plasticizers for lacquers and plastics, impregnating agents for wood, and addition products in the manufacture of lead for pencils.

Products of considerable importance are obtained by reacting polyfunctional polyglycolethers and polyfunctional isocyanates in quantities larger than those required for saturating the hydroxyl groups present. In this way, isocyanate modified polyglycolethers can be obtained by applying twice the equivalent amount of polyfunctional isocyanates. These isocyanate modified polyglycolethers contain free isocyanate groups in the molecule and are suitable for numerous further reactions because of the high reactivity of the free NCO groups. The reaction

2,948,691

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of said products with water may be mentioned by way of example by causing water in form of atmospheric moisture to act at room temperature on thin layers of isocyanate modified polyglycolethers, insoluble films or foils are obtained within a longer or shorter period, depending on the reactivity of the isocyanate employed; the reaction of naphthalene-1,5-diisocyanate at 50 percent of relative atmospheric moisture is complete after about 2 hours. The films or foils thus obtained may have paper-like or rubber-elastic properties; they are distinguished by a remarkable swelling behavior. Complete indifference in aliphatic hydrocarbons renders the new products suitable for application in this field in the art where such property is required, for instance in the coating of gasoline tubes or storage tanks for gasoline. The capability of the new products of swelling in water can be utilized if counter-stresses are required of support materials such as paper, fabrics, and films of high polymeric plastics, to which the films or foils are applied, in contact with water or atmospheric moisture. The swelling of the layer consisting of isocyanate modified polyglycoether on said base materials causes in many cases the material to vault to a larger or lesser extent, thus compensating any counter-stresses. The aforesaid refers, for instance, to carbon paper for typewriters which by suitable treatment with the new products is prevented from being rolled up.

Isocyanate modified polyglycolethers, especially those having a molecular weight higher than 2000, are soluble in water. Solutions thus prepared, however, are not stable because of the high reactivity of the isocyanate group in water. Thickening or gel formation with the increase in molecular weight occurs within intervals of some minutes depending on the solid content of the solution. A proportion of 4 percent of an isocyanate modified polyglycoether prepared from a polyglycoether of a molecular weight of 4030 which is obtained by addition of ethylene oxide to trimethylolpropane, suffices to form a gelatinous mass. The use of smaller quantities results in the thickening of the solution.

The cross-linking by carbamide groups is accompanied with the evolution of carbon dioxide. Such course of reaction may be utilized in the manufacture of cellular materials. Isocyanate modified polyglycolethers are intimately mixed with the amount of water sufficient for reacting the excess isocyanate present, preferably in the presence of alkaline media, for instance, alkali phenolates or more preferably tertiary amines, in quantities of about 2 percent calculated on the isocyanate modified polyglycolethers, optionally with the aid of an emulsifier. The mass soon expands and solidifies to an insoluble cellular material. Of course, cellular materials can also be produced in a single operation step by starting from polyglycolethers which are reacted with the other components. The invention provides innumerable possibilities of variation owing to the great number of polyglycolethers and polyfunctional isocyanates which may be used as starting materials. Cellular materials of the most different physical properties may be obtained by suitable choice of the reactants. All these materials, however, are distinguished, to a larger or smaller extent, by a marked swelling capacity in water and other solvents. Reaction of isocyanate modified polyglycolethers to form insoluble products may further be carried out with aliphatic or aromatic di- or polyamines. For instance, an insoluble film or coating can be produced on a support by subjecting the isocyanate modified polyglycoether applied to the support to vapors of the above said amines, for instance, ethylene diamine. For instance, diaphragms for gasoline pumps can be produced in this manner.

The isocyanate modified polyglycolethers obtained according to the invention may further be utilized in the manufacture of compact plastics. For this purpose, glycols or polyvalent, primary or secondary, alcohols, furthermore diamines or polyvalent, primary or secondary, amines are preferably employed as cross-linking agents

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instead of water. Because of the larger proportion of isocyanate and the different arrangement of the isocyanate in the molecular structure the physical properties of the plastics thus prepared differ from those produced from equivalent amounts of polyfunctional isocyanates.

Furthermore, the isocyanate modified polyglycolethers are valuable intermediate products for a number of further reactions. For instance, N,N'-dialkylaminoethanols may be chemically added without difficulties thus forming basic polyglycolethers. These basic polyglycolethers may be rendered quaternary by means of halides whereby new classes of compounds are made accessible. The use of epichlorohydrin gives rise to terminal alkylene oxide groups which may be used for further reactions. Plastics of new properties can be obtained from dihalides, for instance 1,4-dichlorobutene. By chemical addition of fatty alcohols substances having emulsifying properties are obtained. The aforesaid modifications may be named as examples of reactions which provide new classes of compounds. It is, however, by no means intended to restrict the application of isocyanate modified polyglycolethers as intermediate products.

In the reaction of polyglycolethers and polyfunctional isocyanates a too vigorous reaction and insolubilization of the reaction mixture often take place. Such course of reaction easily occurs when polyglycols containing free alkali from their preparation are employed. A too vigorous reaction and insolubilization are safely avoided by carrying out the reaction of polyfunctional polyglycolethers and polyfunctional isocyanates in the presence of acid reacting substances or substances which are capable of forming acid, for instance, by the action of water or heat. Very small quantities of said substances, say less than 0.5 percent, frequently only 0.05 percent calculated on the polyglycolethers, suffice to secure a uniform course of reaction. Suitable substances for this purpose are, for instance, organic and inorganic acid chlorides such as acetyl chloride, propionyl chloride, oxalyl chloride, adipic acid chloride, benzoyl chloride, phosphorus tri- and pentachloride, phosphorus oxychloride, tin tetrachloride, furthermore hydrohalic acids, inorganic acid anhydrides such as sulfur dioxide and sulfur trioxide. Reference may further be made to butadiene sulfone which decomposes into butadiene and sulfur dioxide at higher temperatures. The action of the aforesaid substances is shown in various directions:

- (1) They prevent the polymerization of the isocyanate group;
- (2) They exert a retarding influence on the speed of reaction between the isocyanate groups and the hydroxyl groups of the polyglycolethers;
- (3) The polymerization inhibiting action on the isocyanate groups is preserved in the end or intermediate product, even after completion of the reaction.

The latter point is of importance in respect of the storing capacity of the isocyanate modified polyglycolethers which can be easily handled provided that atmospheric moisture is excluded.

In those cases where the acid substances which inhibit polymerization and retard reaction velocity will interfere in the further reactions, the action of the said substances can be compensated at any time by addition of alkaline agents, for instance, tertiary amines. These alkaline agents may either be incorporated into the isocyanate modified polyglycolethers or may be caused to act on the isocyanate modified polyglycolethers from outside, for instance in the form of gases. For instance, if on a support a film or foil is to be produced from a stabilized isocyanate modified polyglycoether the reaction with the atmospheric moisture can be substantially accelerated by contacting the isocyanate modified polyglycoether applied to the support with a gaseous atmosphere, for instance, such containing vapors of hexahydromethylaniline.

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The invention is further illustrated by the following examples without being restricted thereto, the parts being by weight.

Example 1

50 parts of a polyglycoether obtained by chemical addition of 8.3 mols of ethylene oxide to 1 mol of trimethylol propane are reacted with 16.8 parts of hexamethylene diisocyanate at 120° C. for two hours. The melt becomes viscous. A light yellow resin is obtained on cooling which is insoluble in hot and cold water and forms viscous solutions in acetone, benzene, chloroform, and ethyl acetate. The resin may be used as addition agent for lacquers and plastics, for instance those prepared on the basis of nitrocellulose.

Example 2

300 parts of a polyglycoether obtained by addition of 9.5 mols of ethylene oxide to 1 mol of trimethylol propane are reacted with 196 parts of phenyl isocyanate. After completion of the exothermic reaction the mixture is stirred at 150° C. for one hour. The resultant viscous oil (481 parts) is insoluble in water but dissolves in organic solvents. The oil is not volatile and compatible with nitrocellulose, cellulose acetobutyrate, cellulose triacetate, benzyl cellulose, polyvinyl acetate, copolymers of vinyl chloride, and polyvinyl acetate, and may successfully be employed for plasticizing said substances. The reaction product has a flash point of 249° C., the point of ignition is 284° C. The product shows good lubricating properties.

Example 3

300 parts of the polyglycoether described in Example 2 are reacted with 266 parts of 6-chlorohexylisocyanate at 120–150° C. until a homogeneous melt has formed which is stirred at 150° C. for another hour. The excess isocyanate is removed in vacuo by heating. 540 parts of an oil of mean viscosity is obtained which is insoluble in water but soluble in organic solvents. The oil is not volatile and compatible with nitrocellulose, cellulose acetobutyrate, cellulose triacetate, benzyl cellulose, chlorinated rubber, polyvinylacetate, copolymers of polyvinylchloride, and polyvinylacetate, and may successfully be employed for plasticizing said products. Furthermore, the oil has good lubricating properties.

Example 4

50 parts of a polyglycoether obtained by addition of 9 mols of ethylene oxide to 1 mol of trimethylol propane are reacted with 34 parts of stearyl isocyanate at 140° C. for 4 hours. The resultant paste forms turbid suspensions in cold water and is insoluble in hot water. The substance may be employed for emulsifying for instance fats, oils, and hydrocarbons in water.

Example 5

Polymeric products of varying solubility properties can be obtained by reacting a polyglycoether prepared from trimethylol propane and ethylene oxide, which has the molecular weight 4030, with hexamethylene diisocyanate. The process of preparing said polymeric product is carried out as follows: 100 parts of the polyglycoether are dehydrated at 150° C. and 1 mm. Hg by treatment in vacuo for one hour, thereupon cooled to 45° C. and 0.25 percent of acetyl chloride is added. 15 minutes after addition of acetyl chloride, hexamethylene diisocyanate is introduced into the melt which is constantly stirred and simultaneously heated to 80° C. After thoroughly mixing the reactants which generally takes about 10 minutes, the mixture is poured into a vessel which may be closed and the reaction is completed in the

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vessel by heating to 80° C. for 6 hours. The products listed in the following table are obtained by the reaction:

Product No.	grams of hexamethylene diisocyanate per 100 grams of polyglycoether	viscosity no. 20 solvents/water	solubility	
			water	methanol
10	3.0	33.9	soluble.....	soluble.....
2	3.7	38.2	do.....	Do.....
3	3.8	51.0	do.....	Do.....
4	3.0	insoluble in cold, soluble in warm or hot water.	Do.....
5	4.0	Do.....
6	4.1	Do.....
7	4.2
8	4.4	insoluble.....

All the above isocyanate modified resins are highly viscous, fibre forming masses in the heat; they are tough at room temperature and show a conchoidal structure. Like the polyglycoether used for their preparation all the products are distinguished by complete insolubility in aliphatic hydrocarbons. The aqueous solutions of the products may be employed as textile assistants and for impregnating wood, especially in the preparation of pencils. Furthermore, the products may successfully be used in the preparation of lead for pencils and as plasticizers for plastics and lacquers.

Example 6

The wax of the molecular weight 4030, which is prepared from trimethylol propane and ethylene oxide, is dehydrated as described in Example 5 and acetyl chloride is added. The wax is then mixed with toluylene diisocyanate (6.48 parts per 100 parts of wax), the mixture is cast into a mold wherein the reaction is completed by heating for 6 hours to 100° C. A cross-linked plastic is obtained which is insoluble in water and organic solvents and shows rubber-elastic properties, especially at temperatures above the softening point of the resin used (48° C.). The product is of importance because of its incapability of swelling in aliphatic hydrocarbons and its swelling capacity in water.

The use of 7.82 parts of naphthalene-1,5-diisocyanate, or of 6.25 parts of hexamethylene diisocyanate per 100 parts of wax results in the formation of similar cross-linked plastics. It is thus possible to produce shaped articles by casting.

Example 7

100 parts of a polyglycoether prepared from trimethylol propane and ethylene oxide, which has a molecular weight of 4030, are reacted with 16.9 parts of naphthalene-1,5-diisocyanate after dehydration and addition of acetyl chloride as described in Example 5. In order to ensure a homogeneous melt the isocyanate is added at a temperature of 125–130° C. and after fusing the isocyanate the melt is heated to 80–100° C. for a further two hours while continuously stirring. The product obtained by the reaction is an isocyanate modified polyglycoether having three reactive isocyanate groups per one mol of polyglycoether. By applying this product in a thin layer from a 75 percent acetone solution to a glass plate, a rubber-elastic film which may be removed from the support is obtained after stirring at room temperature for one and a half to two hours. The film shows remarkable swelling properties which are determined by means of 0.25 mm. thick lamellae of an area of 9 cm.² by swelling at room temperature in the most various solvents which are listed in the table below. As measure for the swelling degree the quotient of the area of the swelled lamella (F) and the area of the lamella prior to swelling (F₀) is given in the table.

Solvents	Swelling Quotient F/F ₀	Film of: polyglycolether, molecular weight 4030, + 16.9 parts by weight of naphthalene-1,6-diisocyanate per 100 grams of polymer	Film of: polyglycolether, molecular weight 8950, + 0.4 parts by weight of naphthalene-1,6-diisocyanate per 100 grams of polymer
water.....	2.05	2.90	
ethanol.....	1.48	1.11	
methanol.....	1.08	2.38	
acetone.....	1.65	2.20	
diethyl ether.....	1.17	1.03	
tetrachloride carbon.....	1.48	1.20	
methylene chloride.....	3.00	4.12	
dimethyl formamide.....	2.67		
benzene.....	1.82	2.71	
gasoline.....	1.03	1.00	
cyclohexane.....		1.00	

Foils showing similar swelling properties may be obtained from the aforesaid polyglycolether and 13 parts of toluylene diisocyanate per 100 parts of wax. The reaction of such diisocyanate modified polyglycolether and atmospheric moisture is preferably carried out at moderately elevated temperatures, for instance at 50° C., since this isocyanate modified polyglycolether crystallizes at room temperature thus causing the formation of films with rough surfaces. This crystallinity is still more noticeable with isocyanate modified polyglycolether of higher molecular weight, for instance such obtained by reacting a polyglycolether of the molecular weight 8950, which is prepared from pentaerythrite and ethylene oxide, with 9.4 parts of naphthalene-1,5-diisocyanate per 100 parts of wax. The films produced from the latter type isocyanate modified polyglycolethers have more noticeable swelling properties (see table), however, without showing principal differences from the above described product produced by means of 60.9 parts of naphthalene-1,5-diisocyanate.

Example 8

100 parts of a polyglycolether of the molecular weight 4030, prepared by addition of ethylene oxide to trimethylol propane, are reacted with 0.5 percent of butadiene sulfone at 150° C. and 1 mm. Hg after dehydration for one hour. The major part of the butadiene sulfone has decomposed after 30 minutes. To remove volatile ingredients vacuum treatment is repeated for a short time until the melt is free of bubbles. Thereupon 14 parts of toluylene diisocyanate are added while continuously stirring at 80° C. and the reaction is completed by heating the melt at the same temperature for another hour. An isocyanate modified polyglycolether containing 3.2 percent of NCO groups is thus obtained. The product is stable provided that atmospheric moisture completely is excluded. Crystallisation occurs at room temperature, the product is liquid at moderately elevated temperatures. The free NCO groups render the isocyanate modified polyglycolether suitable for use as intermediate product in further reactions. The reaction of the product in thin layers with atmospheric moisture to form rubber-elastic films has been described in Example 7. Other effects are attained by stirring the product into water. For this purpose, a solution of the isocyanate in acetone or tetrahydrofuran is preferably employed. Presently after preparation of the aqueous solution the latter solidifies to an insoluble gel. The solidity of the gel increases with the quantity of the isocyanate modified polyglycolether used. When 4 percent of diisocyanate modified polyglycolether is employed a solid oil is obtained whereas 3 percent of diisocyanate modified polyglycolether causes the formation of a thickly viscous liquid. Gel formation is accompanied with the evolution of carbon dioxide which can be perceived by the forma-

tion of bubbles in the gel, especially when larger quantities of the isocyanate are used. The reaction can advantageously be adapted to the thickening of aqueous solutions or emulsions.

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Example 9

The isocyanate modified polyglycolether obtained according to Example 8, which contains 3.2 percent of NCO groups, can successfully be employed in the manufacture of plastics. 100 parts of this isocyanate modified polyglycolether are reacted with 6.8 parts of dimethyl amino ethanol at 80° C. A polyglycolether containing terminal, tertiary nitrogen atoms is thus obtained. By mixing this basic intermediate product with 5 percent of 1,4-dichlorobutane a cross-linked, insoluble plastic is obtained in an exothermic reaction.

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Example 10

100 parts of the isocyanate modified polyglycolether obtained according to Example 8, which contains 3.2 percent of NCO groups, is mixed with 2 percent of water and 2 percent of the prepared product by addition of phenyl isocyanate to N,N'-dimethyl amino ethanol at moderately elevated temperatures at which the product is present in a liquid form. The mass begins to expand by the action of carbon dioxide evolved from the free NCO groups and water, and eventually solidifies to an elastic cellular product. The product has the remarkable property of swelling in water to a material extent whereby an increase in molecular weight by 4 times the weight of the starting material was determined. After drying the swelled sponge the starting material is recovered.

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Example 11

100 parts of an ethylene oxide polymer having the hydroxyl number 11.0 are dehydrated at 150° C. and 1 mm. Hg for one hour and intimately mixed after cooling to 80° C. with hexamethylene diisocyanate in quantities indicated in the table below. The mixture, which becomes distinctly more viscous already after 10 minutes, is filled into a container wherein the reaction is completed by heating to 80° C. for 8 hours. Products of high molecular weight which have higher viscosity numbers than the starting materials are obtained. All the products are soluble in water.

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Text No.	grams of hexamethylene diisocyanate per 100 grams of ethylene oxide polymer	viscosity number measured in water as solvent
untreated polymer.....		17
1.....	1.5	22.9
2.....	2.0	40.9

Example 12

250 parts of a polyglycolether of the hydroxyl number 58.0, which has been obtained by addition of ethylene oxide to pentaerythrite, are reacted with 0.725 part of acetyl chloride and thereafter with 40 parts of toluylene diisocyanate after dehydration by heating in vacuo at 50° C. The reaction is complete after 1 hour's stirring at 80° C. The resultant isocyanate modified polyglycolether contains 3.53 percent of NCO groups. The product shows the same properties, for instance in water, as the diisocyanate modified polyglycolether described in Example 8.

We claim:

1. The process which comprises reacting under substantially anhydrous conditions a polyalkylene ether glycol having a molecular weight greater than 1000 with a molar excess of a compound of the formula



70 wherein R is hydrocarbon.

2. A process for making polymers which comprises reacting a polyalkylene ether of a saturated aliphatic hydrocarbon polyol, said polyalkylene ether having at least two hydroxyl groups per molecule and a molecular weight of at least about 500, and an organic isocyanate containing only hydrocarbon radicals and NCO.

3. The process of claim 2 wherein the said isocyanate is a diisocyanate.

4. The process of claim 2 wherein the said reaction occurs in the presence of an acidic substance.

5. The process of claim 2 wherein the reaction mixture contains a substance capable of engendering acid under the reaction conditions.

6. The process of claim 2 wherein the reaction mixture contains an excess of said isocyanate over that required to react with all of said hydroxyl groups.

7. A process for making polymers which comprises reacting a polyalkylene ether glycol having a molecular weight of at least about 500 and an organic isocyanate containing only hydrocarbon radicals and NCO.

8. The process of claim 7 wherein the said reaction occurs in the presence of an acidic substance.

9. The process of producing polymers which comprises reacting a polyalkylene ether of a saturated aliphatic hydrocarbon polyol, said polyalkylene ether having at least two hydroxyl groups per molecule, and a molecular weight of at least about 500, and an organic isocyanate containing at least two NCO groups, said isocyanate containing only hydrocarbon radicals and NCO, said isocyanate being present in the reaction mixture in an amount larger than that required for reacting with all of the hydroxyl groups of said ether, and reacting the resulting isocyanate-modified polyalkylene ether with a member selected from the group consisting of water and an organic compound containing at least two active hydrogen-containing groups in the molecule, said active hydrogen-containing groups being reactive with isocyanate groups.

10. The process of claim 9 wherein the active hydrogen-containing groups are selected from the group consisting of alcoholic hydroxyl groups, primary amino groups, and secondary amino groups.

11. The process of claim 9 wherein the reaction between the isocyanate and the polyalkylene ether is conducted in the presence of an acidic substance.

12. The process of producing polymers which comprises reacting a polyalkylene ether glycol having a molecular weight of at least about 500, and an organic isocyanate containing at least two NCO groups, said isocyanate containing only hydrocarbon radicals and NCO, said isocyanate being present in the reaction mixture in an amount larger than that required for reacting with all of the hydroxyl groups of said ether, and reacting the resulting isocyanate-modified polyalkylene ether glycol with a member selected from the group consisting of water and an organic compound containing at least two active hydrogen-containing groups in the molecule, said active hydrogen-containing groups being reactive with isocyanate groups.

13. A process for making polymers which comprises reacting a member selected from the group consisting of water and an organic compound containing at least two active hydrogen-containing groups in the molecule, said active hydrogen-containing groups being reactive with isocyanate groups, a polyalkylene ether of a saturated aliphatic hydrocarbon polyol, said polyalkylene ether having at least two hydroxyl groups per molecule and a molecular weight of at least about 500, and an organic isocyanate containing at least two NCO groups, said isocyanate containing only hydrocarbon radicals and NCO.

14. The process of claim 13 wherein the active hydrogen-containing groups are selected from the group consisting of alcoholic hydroxyl groups, primary amino groups, and secondary amino groups.

15. A process for making a cellular material which comprises reacting water, a polyalkylene ether of a satu-

rated aliphatic hydrocarbon polyol, said polyalkylene ether having at least two hydroxyl groups per molecule and a molecular weight of at least about 500, and an organic isocyanate containing at least two NCO groups, said isocyanate containing only hydrocarbon radicals and NCO, said isocyanate being present in an amount in excess over that required to react with all of the hydroxyl groups of said polyalkylene ether.

16. The process of claim 15 wherein the polyalkylene ether has three hydroxyl groups per molecule.

17. The process of claim 15 wherein an acidic substance is present in the reaction mixture.

18. The process of claim 15 wherein an acid-engendering substance is present in the reaction mixture.

19. A synthetic polymer prepared by a process which comprises reacting a polyalkylene ether of a saturated aliphatic hydrocarbon polyol, said polyalkylene ether having at least two hydroxyl groups per molecule and a molecular weight of at least about 500, and an organic isocyanate containing only hydrocarbon radicals and NCO.

20. A synthetic polymer prepared by a process which comprises reacting a polyalkylene ether glycol having a molecular weight of at least about 500, and an organic isocyanate containing only hydrocarbon radicals and NCO.

21. A cellular polyurethane prepared by a process which comprises reacting water, a polyalkylene ether of a saturated aliphatic hydrocarbon polyol, said polyalkylene ether having at least two hydroxyl groups per molecule and a molecular weight of at least about 500, and an organic isocyanate containing at least two NCO groups, said isocyanate containing only hydrocarbon radicals and NCO, said isocyanate being present in an amount in excess over that required to react with all of the hydroxyl groups of said polyalkylene ether.

22. A cellular polyurethane prepared by a process which comprises reacting water, a polyalkylene ether of a saturated aliphatic hydrocarbon polyol, said polyalkylene ether having at least three hydroxyl groups per molecule and a molecular weight of at least about 500, and an organic isocyanate containing at least two NCO groups, said isocyanate containing only hydrocarbon radicals and NCO, said isocyanate being present in an amount in excess over that required to react with all of the hydroxyl groups of said polyalkylene ether.

23. A polymer prepared by a process which comprises reacting a polyalkylene ether of a saturated aliphatic hydrocarbon polyol, said polyalkylene ether having at least two hydroxyl groups per molecule and a molecular weight of at least about 500, water and an organic isocyanate containing at least two NCO groups, said isocyanate containing only hydrocarbon radicals and NCO.

24. A polymer prepared by a process which comprises reacting a member selected from the group consisting of water and an organic compound containing at least two active hydrogen-containing groups in the molecule, said active hydrogen-containing groups being reactive with isocyanate groups, a polyalkylene ether of a saturated aliphatic hydrocarbon polyol, said polyalkylene ether having at least two hydroxyl groups per molecule and a molecular weight of at least about 500, and an organic isocyanate containing at least two NCO groups, said isocyanate containing only hydrocarbon radicals and NCO.

25. The polymer of claim 24 wherein the active hydrogen-containing groups are selected from the group consisting of alcoholic hydroxyl groups, primary amino groups, and secondary amino groups.

26. A polymer prepared by a process which comprises reacting under substantially anhydrous conditions a polyalkylene ether of a saturated aliphatic hydrocarbon polyol, said polyalkylene ether having at least two hydroxyl groups per molecule and a molecular weight of at least about 500 and a molar excess of an organic isocyanate containing at least two NCO groups, said iso-

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cyanate containing only hydrocarbon radicals and NCO.
27. The process of claim 2 wherein the isocyanate is toluylene diisocyanate.
28. The process of claim 2 wherein the isocyanate is naphthalene-1,5-diisocyanate.

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PLAINTIFF'S EXHIBIT 6

U. S. Patent No. 2,527,970, Herman Sokol

Pages 702a to 706a

UNITED STATES PATENT OFFICE

2,527,970

HYDROXY ETHERS AND PROCESS FOR
PRODUCTION THEREOF

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No Drawing. Application June 18, 1945,
Serial No. 600,219

7 Claims. (Cl. 260—615)

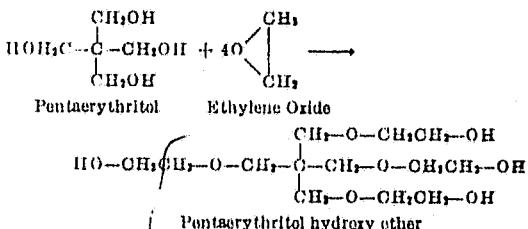
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The present invention relates to the production of hydroxy ethers or ether-alcohols, and more specifically to the production of ethers by the reaction of alkene epoxides (alkene oxides) and aliphatic polyhydroxy compounds. In one of its more specific aspects, the invention relates to a process for the production of hydroxy ethers having high molecular weights by the reaction of propylene oxide or a similar alkene oxide and pentaerythritol or a polypentaerythritol in the presence of an alkaline catalyst to produce ethers in which more than one alkene oxide molecule is reacted with each original hydroxyl radical of the pentaerythritol or polypentaerythritol. The invention also relates, in another of its more specific embodiments, to the novel hydroxy ethers thus produced.

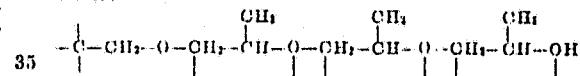
Hydroxy ethers have been produced heretofore by the reaction of alkene oxides and aliphatic hydroxy compounds. The reaction may be conducted without a catalyst (see M. Wittwer, U. S. Patent No. 1,976,677). However, various different catalysts, including boric and sulfuric acids (O. Schmidt and E. Meyer, U. S. Patent No. 1,922,459 and British Patent No. 317,770), alkali-metal alcohohates, alkali-metal salts of lower fatty acids, normal sulfates of polyvalent metals, dialkyl sulfates, hydrosilicates, tertiary amines, pyridine, certain metal oxides, and stannic halides, antimony pentahalides, aluminum halides, zinc halides, ferric halides, and other metal halides (K. E. Marple, E. C. Shokal and T. W. Evans, U. S. Patent No. 2,327,053), have been suggested for facilitating the reactions. Other specific catalysts for the reactions, which are disclosed in the copending applications of Philip I. Bowman, Robert H. Barth and Harry Burrell, Serial No. 474,328, filed February 1, 1943, which has issued as Patent No. 2,401,743, and Serial No. 545,888, filed July 20, 1944, now abandoned, are acetic acid, acetic anhydride, pentaerythritol diacetate, pentaerythritol tetraacetate, benzoyl chloride and the double compound of boron fluoride and ethyl ether. When the reaction of an alkene oxide and pentaerythritol is conducted in the absence of a catalyst or in the presence of such catalysts as have heretofore been specified, the products are generally the expected hydroxy ether and varying proportions of polymers of the alkene oxide. Generally not more than one alkene oxide mole-

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cule reacts with each hydroxyl radical of the pentaerythritol. In the case of ethylene oxide and pentaerythritol the reaction may be represented as:



When certain catalysts are used the product is a mixture of the expected pentaerythritol hydroxy ether and varying amounts of polymers of ethylene oxide. From the hydroxyl content of such a mixture it might be concluded that more than one ethylene oxide molecule had reacted with each of the original hydroxyl radicals of the pentaerythritol. For example, in the case of a reaction in which a quantity equivalent to 3 molecules of propylene oxide was unrecovred for each original hydroxyl radical of the pentaerythritol, the hydroxy ether might be expected to be as represented by the following schematic formula, in which all four of the original methylo radical of the pentaerythritol have been replaced by the represented hydroxy ether radical that is attached to the central or nuclear pentaerythritol carbon atom:



(The molecular weight of such a compound is approximately 830.) However, the molecular weight of the mixed product is much lower than would correspond to such a compound. As far as known, such pentaerythritol and polypentaerythritol hydroxy ethers having molecular weights corresponding to compounds in which two or more alkene oxide molecules have reacted with each original hydroxyl radical of pentaerythritol or a polypentaerythritol are not known and cannot be produced by processes heretofore known or described in the art.

The principal object of the present invention is to provide a process for the production of hy-

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droxy ethers having high molecular weights which are products of the reaction of an alkene oxide and a polyhydric alcohol in which at least 2 molecules of alkene oxide are reacted with each of the original hydroxyl radicals of the polyhydric alcohol. It is a further more specific object of the invention to provide a process for the production of such hydroxy ethers of pentaerythritol and polypentaerythritols.

A further object of the present invention is to provide compounds having high molecular weights which are reaction products of pentaerythritol and polypentaerythritols and alkene oxides in which at least 2 molecules of alkene oxide are reacted with each of the original hydroxyl radicals of the pentaerythritol or polypentaerythritol.

Other objects and advantages of the invention, some of which are referred to more specifically hereinafter, will be apparent to those skilled in the art to which the invention pertains.

As used in this specification, the term "polypentaerythritol" is to be understood to include dipentaerythritol, tripentaerythritol and mixtures thereof, such as "pleopentaerythritol" (a mixture of dipentaerythritol and tripentaerythritol having a melting range of 230° to 240° C. and a hydroxyl content of approximately 33%).

I have discovered that propylene oxide and similar alkene oxides may be reacted with polyhydric alcohols such as pentaerythritol and polypentaerythritols to produce compounds corresponding to a reaction of at least 2 molecules of alkene oxide with each original hydroxyl radical of the polyhydric alcohol. In order to effect such a reaction it is necessary to use a strongly alkaline-reacting catalyst such as sodium metal, sodium hydroxide, potassium hydroxide, sodium methoxide and similar compounds. Only a small proportion of catalyst is required. It is furthermore necessary to conduct the reaction under substantially anhydrous reaction conditions since I have found that small but significant amounts of water favor the polymerization of the alkene oxide and hinder or suppress the desired reaction of the alkene oxide with the polyhydric alcohol. Furthermore, it is necessary to use xylene or another inert organic solvent which dissolves both the alkene oxide and the desired hydroxy ethers but which does not dissolve substantial amounts of the pentaerythritol or polypentaerythritol. Such inert solvent is preferably one with a low vapor pressure and a low molecular weight. By use of such an inert solvent the reaction may be conducted at a lower pressure. The solvent is used in substantial amounts but need not be used in a greater than equimolecular amount based on the alkene oxide.

Hydroxy ethers of my invention and processes for their production are illustrated in the examples which follow hereinafter:

Example 1.—Hydroxypropyl ether of dipentaerythritol (two propylene oxide per hydroxyl)

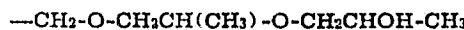
Into a one-liter, high-pressure, rocker-type steel bomb were charged 50.8 grams (approximately 0.2 mol) of dipentaerythritol, 151 grams (approximately 2.6 mols) of propylene oxide and 276 grams (approximately 2.6 mols) of xylene. The reaction mixture contained less than 0.1% water by weight. Approximately 0.3 gram of sodium metal was added and the mixture was heated with agitation to a temperature of 175° C. during the course of approximately 4 hours. The pressure rose to 90 pounds per square inch and

then gradually fell to 40 pounds per square inch. Continued heating produced no further decrease in pressure.

After cooling the bomb to room temperature, its contents were removed and subjected to distillation at reduced pressure to remove the xylene and unreacted propylene oxide. Distillation was continued until no further distillate was obtained at a residue temperature of 100° C. and at a pressure of 5 mm. of mercury. The residue was a clear, light-brown-colored oil which weighed 191 grams and had the following characteristics:

	Observed	Calculated
Molecular weight.....	522	550
Hydroxyl value.....per cent.....	11.0	10.7
Viscosity (25° C.).....poise.....	.65	

In the "calculated" column hereinabove are entered the values for the respective characteristics of a compound corresponding to dipentaerythritol in which each of the six methylol ($-\text{CH}_2\text{OH}$) radicals has been replaced by the radical



The calculated values referred to hereinafter in the other examples were computed in a similar manner.

Polymerization of propylene oxide under identical reaction conditions..

In order to determine what happens to propylene oxide under the actual reaction conditions used in the foregoing examples when pentaerythritol or a polypentaerythritol are not present, the following results are typical of repeated experiments that check each other very closely:

A mixture of 145 grams (approximately 2.5 mols) of propylene oxide and 266 grams (approximately 2.5 mols) of xylene containing approximately 0.5% by weight of water was charged to a 1-liter, high-pressure, rocker-type bomb. Approximately 0.3 gram of sodium metal was added and the agitated mixture was heated slowly to a temperature of 175° C. during a period of approximately 4 hours. The pressure rose to 185 pounds per square inch and then dropped gradually to 100 pounds per square inch. Continued heating produced no further reduction of the pressure.

After cooling the bomb to room temperature, its contents were removed and subjected to distillation at reduced pressure to remove the xylene and unreacted propylene oxide. The distillation was continued until no further distillate was obtained at a temperature of 100° C. (in the residue) and at a pressure of 5 mm. of mercury. The residue was a clear, light-brown-colored oil which weighed 120 grams and had the following characteristics:

Molecular weight	522
Hydroxyl value	per cent.....
Viscosity (25° C.)	poise.....

In view of this result it is obvious that the products of Example 1 hereinbefore and of the examples hereinafter are not simply polymers of propylene oxide but are new chemical entities.

One mol (254 g.) of dipentaerythritol, 30 mols (1320 g.) of ethylene oxide and 2 grams of a catalyst were heated together in a steel autoclave to a temperature of 175° C. The heating was conducted in such manner that approxi-

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mately 5 hours were required to reach 175° C. and the mixture was maintained thereafter at 175° C. for a period of approximately 8 hours. The reaction mixture was allowed to cool and the unconsumed ethylene oxide was distilled from the reaction mixture. The residue was weighed and analyzed.

In the following table are given the weights of the products obtained when different catalysts were used (in each case 2 grams of catalyst were used) and the hydroxyl contents and molecular weights of the resulting products. On the assumption that all of the unrecovered ethylene oxide reacted with the dipentaerythritol and not with itself to form polymers the theoretical molecular weight of the resulting assumed product in each case was calculated and such values are entered in the table for purposes of comparison. The weight of the product and the hydroxyl value of the product checked closely the composition of the assumed product. It is to be noted, however, that the observed molecular weights of the products did not check the theoretical molecular weights of the assumed products.

No.	Catalyst	Weight of Product, in grams	Hydroxyl Content of Product, per cent by weight	Composition of Assumed Product; Ratio of Dipentaerythritol to Ethylene Oxide	Theoretical Molecular Weight of Assumed Product	Observed Molecular Weight of Actual Product
1.	Boric oxide.....	635	17.5	1:9	650	328
2.	Double compound of boron fluoride and ethyl ether (45% BF ₃).....	700	15.1	1:12	782	201
3.	Benzoyl Chloride.....	1,212	16	1:18	1,046	448
4.	Acetyl anhydride.....	1,442	8.3	1:24	1,310	573
5.	Pentaerythritol diacetate.....	1,630	7.5	1:30	1,674	600

The calculated weight of hydroxy ether which should result from the reaction of 1 molecule of dipentaerythritol and 6 molecules of ethylene oxide (1 ethylene oxide molecule per hydroxyl radical of the dipentaerythritol) is approximately 518 and its hydroxyl content is 20.0%. It is evident that the products obtained in the foregoing reactions and which are listed in the table contain no substantial amounts of products corresponding to reaction products having more than 6 molecules of ethylene oxide per molecule of dipentaerythritol and, from the average molecular weights of the products, it is obvious that they contain substantial amounts of polymers of ethylene oxide.

Example 2.—Hydroxypropyl ether of dipentaerythritol (four propylene oxide per hydroxyl)

A charge consisting of 25.4 grams (approximately 0.1 mol) of dipentaerythritol, 145 grams (approximately 2.5 mols) of propylene oxide, 265 grams (approximately 2.5 mols) of xylene and 0.3 gram of sodium metal was reacted and treated as in Example 1. The maximum pressure developed during the reaction was 95 pounds per square inch.

The product obtained weighed 162 grams and was a clear, brown oil, which had the following characteristics:

	Observed	Calculated
Molecular weight.....	1,627	1,646
Hydroxyl value..... per cent	7.9	6.2
Viscosity (25° C.)..... poises	18	70

Example 3.—Hydroxyethyl ether of pentaerythritol (three ethylene oxide per hydroxyl)

A charge consisting of 27.2 grams (approxi-

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mately 0.2 mol) of pentaerythritol, 114.4 grams (approximately 2.6 mols) of ethylene oxide, 276 grams (approximately 2.6 mols) of xylene and 0.6 gram of sodium hydroxide was reacted and treated as in Example 1. The maximum pressure developed during the reaction was 195 pounds per square inch.

The product thus obtained weighed 134 grams and was a clear, yellow-colored oil having the following characteristics:

	Observed	Calculated
Molecular weight.....	628	664
Hydroxyl value..... per cent	11.1	10.3

Example 4.—Hydroxybutenyl ether of dipentaerythritol (one butadiene monoxide per hydroxyl)

A charge consisting of 102 grams (approximately 0.4 mol) of dipentaerythritol, 196 grams (approximately 2.8 mols) of butadiene monoxide, 296 grams (approximately 2.8 mols) of xylene and 0.3 gram of sodium metal were reacted and treated as in Example 1. The maximum pressure

developed during the reaction was 85 pounds per square inch.

The product weighed 273 grams and was a clear reddish-brown-colored oil having the following characteristics:

	Observed	Calculated
Molecular weight.....	1,866	874
Hydroxyl value..... per cent	16.1	14.1
Viscosity (25° C.)..... poises	358	230
Iodine number.....	230	226

From the observed molecular weight it appears that the product is a trimer of the expected ether.

In the foregoing examples the reactions were conducted under substantially anhydrous conditions of reaction. As hereinabove stated, it has been found that the presence of water favors the polymerization of the alkene oxide. Although some water may be present, the yield of the desired product may be substantially affected.

Although xylene was the inert liquid used in the foregoing examples, other inert organic solvents which dissolve both the alkene oxide and the desired hydroxy ethers but which do not dissolve substantial amounts of pentaerythritol or poly-pentaerythritols may be used. Such solvents are, for example, petroleum naphtha fractions, toluene and other aromatic hydrocarbons and the like. The inert solvents which are preferred are those which have low vapor pressures and low molecular weights. Xylene is a preferred solvent in this respect. The amount of solvent which is used should be sufficient to dissolve the alkene oxide and to provide control of the pressure to the desired extent. Normally amounts greater than an equimolecular proportion based on the weight of the alkene oxide need not be used.

In effecting the reaction the alkene oxide should preferably be used in considerable excess of the stoichiometrical amount. In this manner some control of the number of alkene oxide groups which enter into the formation of the product may be obtained. As shown in Examples 1 and 2, approximately 2 mols of alkene oxide react per hydroxyl group of dipentaerythritol when approximately 13 mols of alkene oxide are present for each mol of dipentaerythritol, whereas 4 mols of alkene oxide react per hydroxyl group when 25 mols of alkene oxide are present for each mol of dipentaerythritol.

Alkaline catalysts which may be used are sodium metal, sodium hydroxide (whose uses are illustrated in the examples), sodium methoxide, potassium hydroxide, and generally alkali metals, alkali-metal oxides and alkali-metal hydroxides. The proportion of catalyst in the reaction mixture is not critical and may be varied considerably. Only a small proportion, as illustrated in the examples, need be used. When acid catalysts or catalysts such as boric oxide, boric acid, boron fluoride, benzoyl chloride, acetic anhydride, or esters such as pentaerythritol diacetate are used, the product is apparently substantially a derivative in which not more than 1 alkene oxide is reacted per hydroxyl group of the polyhydric alcohol.

Although the reaction is applied hereinabove to the preparation of pentaerythritol and poly-pentaerythritol derivatives, it may be applied to other polyhydric alcohols having more than 3 hydroxyl radicals per molecule.

Derivatives of alkene oxides other than ethylene oxide, propylene oxide and butadiene monoxide may be prepared in similar manner, as is obvious. Such additional alkene oxides which may be used are butylene oxide, pentene oxides and aryl-substituted alkene oxides such as styrene epoxide.

The hydroxy ethers of the present invention are readily dehydrated to produce olefin ethers. Accordingly care must be exercised to control the reaction and prevent the temperature from rising to an extent such as to effect dehydration of the desired compound. It is for this reason that the compounds cannot be readily separated by distillation from any alkene oxide polymers that may be formed in the reaction. In conducting the reaction, if a product that is substantially free from alkene oxide polymers is required, it is desirable to observe all precautions specified herein in order that difficult separations of the desired products from the alkene oxide polymers may be avoided.

Although, as shown in the foregoing examples and comparative results, the products of my invention are apparently substantially free from polymers of alkene oxides and consist essentially of polyhydric alcohols in which each of the original hydroxyl radicals of the polyhydric alcohol has been replaced by a hydroxy ether radical containing at least 2 alkene oxide nuclei, such as the radicals $-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)-\text{O}-$

$\text{CH}_2\text{CH}(\text{CH}_3)-\text{O}-\text{CH}_2\text{CHOH}-\text{CH}_3$ and the like, it is to be understood that the invention is not to be thus restricted. The products of my invention are novel and may have compositions and constitutions which are quite different from those referred to herein. Accordingly, because of the difficulty in separation, isolation and identification of such products or individual components thereof, the specification

and the claims are to be interpreted in the light of these facts, that is, the claims are to be given the broadest interpretation of which they are capable and compounds which are referred to herein as having a presumed constitution, formula or composition are to be regarded as having such other composition, constitution or formula as they actually possess.

The hydroxy ethers of the present invention are useful as solvents and plasticizers for various plastic organic substances such as zein and others characterized by a plurality of C—O—C linkages, such as cellulose ethers, cellulose nitrate, cellulose acetate, polyvinyl alcohols, polyvinyl acetals, phenol-aldehyde resins, urea-formaldehyde resins and the like. They generally possess hydrophilic properties and are useful as emulsifying agents, wetting agents, interface-modifying agents and may be used as antispattering agents for oleaginous and fatty materials. These hydroxy ethers may also be used for the breaking of petroleum-water emulsions. As plasticizing agents for plastic substances they exhibit properties similar to the hydroxy ethers disclosed in the copending applications of Philip I. Bowman, Robert H. Barth and Harry Burrell, Serial No. 474,328, filed February 1, 1943 (Patent No. 2,401,743), and Serial No. 545,888, filed July 20, 1944.

Inasmuch as the foregoing specification comprises preferred embodiments of my invention, it is to be understood that the invention is not limited thereto and that modifications and variations may be made therein without departing substantially from the invention, whose scope is to be limited solely by the appended claims.

I claim:

1. A process for the production of a hydroxy ether by the condensation of ethylene oxide and pentaerythritol, which hydroxy ether is the compound resulting from the condensation of at least eight and not more than sixteen molecular proportions of ethylene oxide with each molecular proportion of pentaerythritol, which comprises heating pentaerythritol with a stoichiometrical excess of ethylene oxide reactive to form said compound at a superatmospheric pressure under essentially anhydrous reaction conditions in the presence of a strongly alkaline catalyst selected from the group consisting of alkali metals and alkali-metal oxides and hydroxides, and in the presence of an inert common solvent for ethylene oxide and said compound but in which pentaerythritol is substantially insoluble.

2. A process for the production of a hydroxy ether by the condensation of propylene oxide and pentaerythritol, which hydroxy ether is the compound resulting from the condensation of at least eight and not more than sixteen molecular proportions of propylene oxide with each molecular proportion of pentaerythritol, which comprises heating pentaerythritol with a stoichiometrical excess of propylene oxide reactive to form said compound at a superatmospheric pressure under essentially anhydrous reaction conditions in the presence of a strongly alkaline catalyst selected from the group consisting of alkali metals and alkali-metal oxides and hydroxides, and in the presence of an inert common solvent for ethylene oxide and said compound but in which pentaerythritol is substantially insoluble.

3. A process for the production of a hydroxy ether by the condensation of propylene oxide

and dipentaerythritol, which hydroxy ether is the compound resulting from the condensation of at least twelve and not more than twenty-four molecular proportions of propylene oxide with each molecular proportion of dipentaerythritol, which comprises heating dipentaerythritol with a stoichiometrical excess of propylene oxide reactive to form said compound at a superatmospheric pressure under essentially anhydrous reaction conditions in the presence of a strongly alkaline catalyst selected from the group consisting of alkali metals and alkali-metal oxides and hydroxides, and in the presence of an inert common solvent for ethylene oxide and said compound but in which dipentaerythritol is substantially insoluble.

4. A process for the production of a hydroxy ether by the condensation of an alkene oxide and a polyhydric alcohol selected from the group consisting of pentaerythritol and dipentaerythritols, which hydroxy ether is the compound resulting from the condensation of at least two and not more than four molecular proportions of the alkene oxide to each molecular proportion of hydroxyl radical present originally in the polyhydric alcohol, which comprises heating the polyhydric alcohol at a superatmospheric pressure under substantially anhydrous reaction conditions with a stoichiometrical excess of the alkene oxide reaction to form said compound dissolved in an inert solvent in which pentaerythritol and polypentaerythritols are substantially insoluble in the presence of a strongly alkaline catalyst selected from the group consisting of alkali metals and alkali-metal oxides and hydroxides.

5. An ether-alcohol consisting of a condensation product of an alkene oxide and an alcohol selected from the group consisting of pentaerythritol and polypentaerythritols in which each of the hydroxyl radicals originally present in the alcohol has been replaced by a radical formed by the condensation of at least two but not more than four alkene oxide molecules, said condensation being carried out in the presence of a solvent in which pentaerythritol and polypentaerythritols are substantially insoluble, and in the presence of a strongly alkaline catalyst under essentially anhydrous reaction conditions.

6. A process for the production of a hydroxy ether by the condensation of an alkene oxide and a polyhydric alcohol selected from the group consisting of pentaerythritol and dipentaeryth-

ritols, which hydroxy ether is the compound resulting from the condensation of at least two and not more than four molecular proportions of the alkene oxide to each molecular proportion of hydroxyl present originally in the polyhydric alcohol which comprises heating the polyhydric alcohol at a superatmospheric pressure under substantially anhydrous reaction conditions with the stoichiometrical excess of the alkene oxide reactive to form said compound, said alkene oxide being dissolved in an inert common solvent for the alkene oxide and said compound but in which pentaerythritol is substantially insoluble, and in the presence of a strongly alkaline catalyst.

7. A process for the production of a hydroxy ether by the condensation of an alkene oxide and a polyhydric alcohol selected from the group consisting of pentaerythritol and polypentaerythritols, which hydroxy ether is the compound resulting from the condensation of at least two and not more than four molecular proportions of the alkene oxide to each molecular proportion of hydroxyl present originally in the polyhydric alcohol, which comprises heating the polyhydric alcohol at a superatmospheric pressure under substantially anhydrous reaction conditions with the stoichiometrical excess of alkene oxide reactive to form such compound, said alkene oxide being dissolved in xylene, and in the presence of a strongly alkaline catalyst.

HERMAN SOKOL.

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35 The following references are of record in the file of this patent:

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	Number	Name	Date
40	1,971,662	Schmidt	Aug. 28, 1934
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	2,094,100	Dreyfus	Sept. 28, 1937
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45	2,253,723	Moore	Aug. 26, 1941
	2,327,053	Marple	Aug. 17, 1943
	2,355,823	Schlegel	Aug. 15, 1944

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	Number	Country	Date
50	317,770	Great Britain	Aug. 19, 1924
	605,973	Germany	Nov. 22, 1934

PLAINTIFF'S EXHIBIT 7B

Bayer, Otto "Industrial Application of the Diisocyanates",
Angewandte Chemie, Vol. 59: 257-272 (Sept. 1947)
(Excerpts, pages 1-31, 41)

Pages 707a to 739a

M-106

707a

INDUSTRIAL APPLICATION OF THE DIISOCYANATES

In order to further promote the industrial application of the organic diisocyanates in American industry, Monsanto Chemical Company herewith makes available an English translation of a very interesting and complete article:

Das Di-Isocyanat-Polyadditionsverfahren (Polyurethane)

(THE DIISOCYANATE POLYADDITION METHOD-POLYURETHANE)

by Prof. Otto Bayer

Farbenfabriken Bayer, Leverkusen

Angewandte Chemie, 59:257-272

Translated by Dr. C. E. PRETZELL

Other literature relating to the Isocyanates available from Monsanto Chemical Co.: Technical Bulletin P-125 - Isocyanates.

ANGEWANDTE CHEMIE

Ausgabe A 59. Jahrgang Nr. 9. Seite 257-272.

September 1947

THE DIISOCYANATE POLY-ADDITION METHOD (POLYURETHANE)

comprehensive description of a new principle to build
up compounds with higher molecules (1937-1945)

by

Professor Dr. Otto Bayer, Farbenfabriken Bayer, Lever-
kusen a/Rh.SURVEY:

Preparation of compounds with high molecular weight.

Characteristics of the condensation method.

Characteristics of the polymerization method.

Principles of the diisocyanate poly-addition method.

Linear polyurethane.

Fibers and thermoplasts.

Linear mixed polyurethanes (leather-like materials).

Patent situation.

Polyureas.

Reticulated polyurethane.

Desmophen-Desmodur lacquers.

Table of the most used diisocyanates (Desmodur).

Table of the most used polyoxy compounds (Desmophen).

Molding compounds.

Foaming materials (Maltopren).

Adhesives (Polystal).

Drying oils (Urethane-linseed oil).

Materials of caoutchouc elasticity.

Tanning materials.

Cellulose + Isocyanates.

NOTE: The footnotes are inserted in parenthesis in the text instead of having them appear at the foot of a page which is difficult to arrange properly.

Diverse new fields of application.

Bifunctional compounds on the basis of isocyanate.

Preparation of the initial materials.

Diisocyanates

Diamines and glycols.

PREPARATION OF COMPOUNDS WITH HIGH MOLECULAR WEIGHTS.

Synthetic high molecular compounds are made in two fundamental ways, either through

- a) condensation or
- b) polymerization.

The characteristics of the condensation method are:

1. A large number of small molecules with at least two functional groups, react with each other under cleavage of a reaction participant with lower molecular weight, as water, hydrochloric acid, NaCl, alcohol, etc.

2. For the formation of the macromolecular compound, in many cases quite robust conditions are applied to the reaction, as; for example, high temperatures, condensation agents, etc. Consequently the synthetics obtained mostly represent mixtures of the most varied condensation stages, even of cracking stages.

3. For the condensation reaction, the possibility is remarkable and valuable to catch intermediary stages of the condensation and to react these to the finish under permanent molding, either as molded articles, casting resins, or infusible lacquer coatings. Mixed condensates can also be made from the most varied preliminary condensation products.

The Thiokols, for instance, from $\text{ClCH}_2\text{CH}_2\text{Cl} + \text{Na}_2\text{S}_4,5$, are typical condensation products in the series of the two-dimensional linear high polymers, also the super-polyamides which are obtained with a molecular weight of 10,000 from condensation of adipic acid and hexamethylene diamine. Furthermore, as examples in the group of the most important three-dimensional, viz., completely reticulated plastics, the finish-hardened Bakelites, the

urea-formaldehyde resins, the glyptals, etc. may be mentioned.

The character of the polymerization reaction is different from the condensation method by:

1. the seemingly smooth addition of a large number (up to 5000 in a linear construction) of molecules of monomer compounds to each other into the high molecular polymerizate, which has the same percentage composition as the monomers;

2. being able to practically start only from reactive vinyl compounds or dienes and to produce from these either linear or reticulated polymers which have all been formed through direct C-C-linkage. The polymerization is an extremely sensitive reaction which takes place through an activated condition (radical) or through a shifting of an activated hydrogen from molecule to molecule of the monomer. Contrary to the condensation reaction, the polymerization proceeds in an extremely mild way. Kinetically it is purely a chain reaction;

3. the fact that the copolymerization of two or three different polymerizable compounds, while rendering a wide possibility of variations (Igelite, Buna, etc.) practically excludes high molecular construction by means of hetero-atoms. So far, polymerization reactions through hetero-atoms were limited to several special cases as, for example, the polymerization of ring systems with a high tension (ethylene oxide, tetrahydrofuran, ethylene imine and caprolactam);

4. the typical property of the polymerization reaction to only permit the obtaining of its finished product and not of reactive intermediary stages as in the condensation reaction. It is not possible to start from di- or tri- or tetramers and to polymerize these further into highly polymerized compounds, either with each other or with the monomers. On the contrary, these intermediary stages, if isolated, act frequently even as polymerization poisons, as, for example, the polymerization of isobutylene to Opanol.

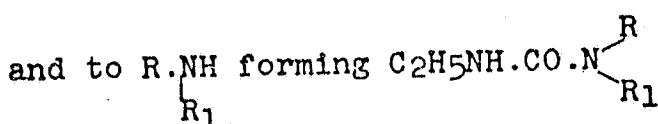
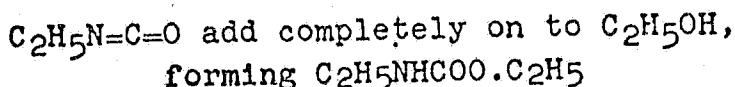
Although the perplexing abundance of the synthetics is practically produced by these two fundamental reactions, a universal method which combines the possibilities and advantages of the classical processes has been lacking.

This method would have to offer the ability to catch any intermediary stage in addition reactions which start from any compounds of lower or higher molecular weight whatsoever or from preliminary condensates or from polymerizates with bi- and poly-functional groups, thus building up macro-molecules with the desired properties. This new desirable method would also have to be strongly exothermal, quantitative, not applying catalysts, and proceeding at normal temperature. The connecting link would have to be stable, neutral and not hydrophilic (as ether or amino groups). These requirements seemed hard to fulfill.

In 1937 a reaction was found in the so-called polyurethane- or diisocyanate-poly addition process, which is still under extensive investigation, which has far surpassed all expectations.¹⁾

(Footnote 1: D.R.P. 728981, Nov. 11, 1937. Inventors: O. Bayer, H. Rinke, W. Siefken; Leverkusen and L. Orthner u. Schild, Hoechst. The D.R.P. and the other foreign patents were later on limited to the addition of poly-functional isocyanates to OH and NH₂-groups in order to clearly demonstrate and characterize the new method as poly-addition. The corresponding Ital. Pat. 367704, however, corresponds to the original German wording and also comprises the reaction with polycarboxylic acids under cleavage of CO₂, leading to poly-amides. Compare Chem. Zentralblatt, 1940, I, 2556. The statements in, "Synthetic Fibre Development in Germany", 1946 on p. 489 and 496 on the history of invention of polymethanes are erroneous and based on a misunderstanding.)

The bases of the new method are the following: Wurtz had already found in 1848 that mono-isocyanates, for example,



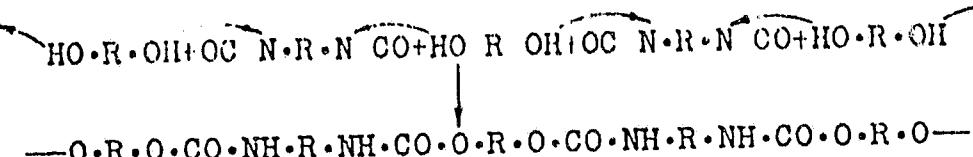
This addition to the N-atom of the isocyanate group proceeds under shifting of the hydrogen atom of the hydroxy or amino group respectively. A. W. Hofmann confirmed in

1849 these observations in the aromatic series with the phenyl isocyanate. If these quantitative and strongly exothermal reactions of addition were to be utilized in the plastics chemistry, it was necessary to prepare the di- and poly-isocyanates and to add these to glycols, diamines, polyoxy or polyamino compounds.²⁾

(Footnote 2: The fundamental idea was developed on 3/26/37. On 10/20/37, O. Bayer called attention to this work at a scientific meeting for synthetics of the I.G. in Frankfurt. L. Orthner remarked that he also intended to prepare linear polymers in the same manner, but he and Schild have limited their research to some preliminary experiments. In 1941 Lieser and Makura, Liebigs Ann. Chem. 548,226, published investigations which were based on the same idea, after publication of the first fundamental patents of O. Bayer, Liebigs Ann. Chem. 549,286, and Lieser, same 550,301. These experiments did not result in any definable and useful products because Lieser and Makura worked only with the easily decomposable diacyl diisocyanates
 $O=C=N \cdot CO \cdot X \cdot CO \cdot N=C=O$.

(Cont. of footnote: It was intentional that the application of di-mustard oils was not patented because they are much less reactive. 1,4-butane diol does not react before ca. 130°C. with 1,6-hexane di-mustard oil forming COS. With diamines the di-mustard oils react in H₂O solution very vigorously forming colorless (reticulated) thioureas which melt under decomposition. Although these analogous sulfur compounds do not show any technical applicability, they have later been covered by patents by several parties. Di-mustard oils can easily be prepared from diamine chloro hydrates in water solution by reaction with 2,2 mol CSCl₂ in benzene solution + CaCO₃. S=C=N(CH₂)₄·N=C=S, m.-p. = 31°, b.-p. 0.2 = 135°C; S=C=N(CH₂)₆·N=C=S, m.-p. 2°, b.-p. 0.2 = 163°C. 1,3 phenylene-di-mustard oil, m.-p. = 4-6°, b.p. 14 = 140°C.

The simplest formulation of the reaction of a diisocyanate with a glycol demonstrates already that this reaction can be compared to a large degree with the normal polymerization reaction:



An essential difference against the usual polymerization process exists by the linkages of molecules not taking place through carbon atoms but through the hetero atoms O and N. With the enormous abundance of the polyoxy compounds alone, the new process is of a much larger applicability than the combined condensation and polymerization processes.

If in the simplest case glycols are applied, linear and fusible polyurethane are obtained. Starting, however from tri- and higher valent alcohols of a medium to higher molecular weight, completely reticulated and infusible masses are the final result. The new method permits for the first time, depending on the application of aromatic or of short or long chained aliphatic components and also on the degree of reticulation, production of synthetics with practically any desired properties and a completely clear chemical structure.

In fact, it is now possible to "construct" high molecular compounds, like a builder, by starting from defined polyoxy compounds of any desirable form without difficulties.

The following scheme will demonstrate this fact:

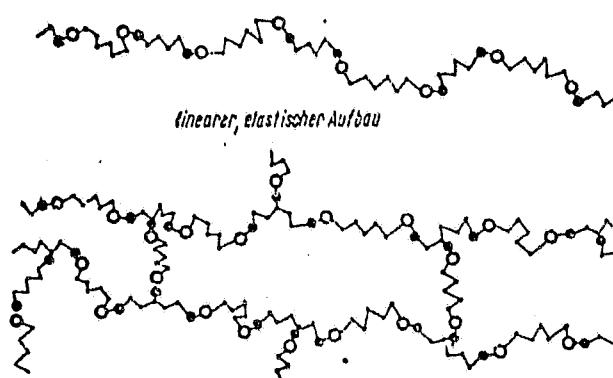


Fig. 1-a
Linear, elastic construction
and
Elastic reticulation

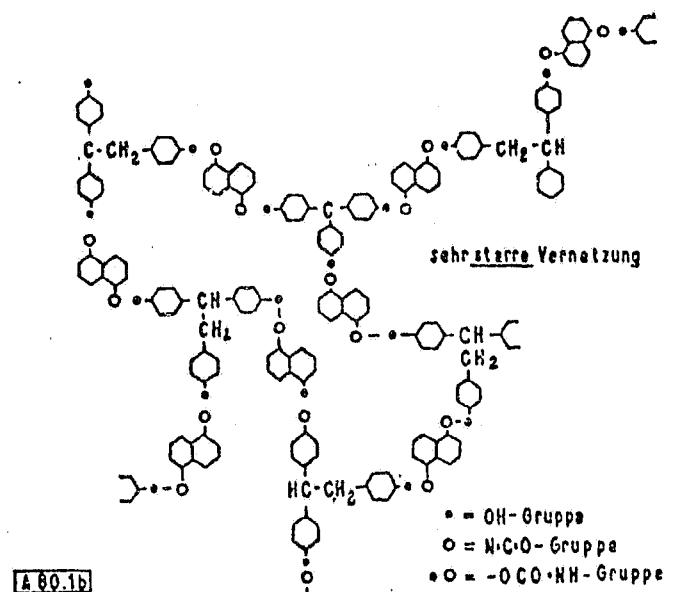


Fig. 1-b
Very rigid reticulation

LINEAR POLYURETHANE

Fibers and Thermoplasts

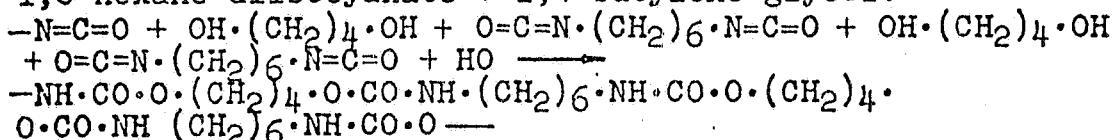
After the work of Carothen on the super-polyamides became known, the most urgent problem was to create something similar or even better which was to be independent from the DuPont patent.

The special case of addition of diisocyanates to glycols and diamines was therefore the first research to be done. By this method linear, high molecular polyurethane and polyureas which could be spun were to be obtained.³⁾

(Footnote 3: The general character of the new process was completely obvious. The first experiment was the reaction of dianisidine diisocyanate with a phenolic resin.)

(Footnotes 4, 5 and 6 concern the names of co-workers.)

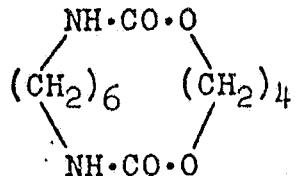
The linear polyurethane thus obtained, proved to be quite many-sided synthetics with qualities which were partially superior to the qualities of super-polyamides. Of the large number of the linear polyurethanes which were made, only a few characteristic ones may be mentioned. The technically easiest accessible and at the same time the most valuable polyurethane is made from 1,6-hexane diisocyanate + 1,4-butylene glycol.



The starting materials have to be of the highest purity and must be applied in molecular proportion in order to avoid breaking of the chain, and can be "poly-added" in a diluent as well as directly by mixing. (D.R.P. Aplic. I. 70685). The formation of polyurethane proceeds in a strongly exothermal reaction (52 Kal. per mol. or 208 Kal. per kg. polyurethane) and is a reaction of the second order.

If one mol of hexane diisocyanate + one mol 1,4-butylene glycol are heated in a monochlorobenzene solution for about one hour a polyurethane separates with a yield of ca. 98% and a molecular weight of 8-9000 as a fine, sandy, completely colorless powder⁷).

(Footnote 7: Compounds of a lower molecular weight remain in solution and also a compound with 16 members and m.-p. 164°C.



(End of Footnote)

By means of special agitators it is possible to run the diisocyanate directly into the glycol without a diluent. The temperature has to be raised to 200°C. in this case in order to obtain a homogenous fusion. In the technical operation this fusion is subsequently extruded through nozzles in the form of ribbons, cords, bristles or fibers. Contrary to the polyamides these compounds can be processed in open vessels because the access of air oxygen does not color the fused polyurethane brown. Nevertheless, a small addition of anti-oxidants in the finished materials is advantageous.

Variations in the molecular proportions of the components, extension of the duration in solution, removal of the reaction heat from the fusion, simultaneous application of mono-functional, viz. chain breaking, components permit varying the molecular weight of the polyurethane in certain limits. Its K-value is normally 53-65, corresponding to an average molecular weight of about 7000-12,000. (10,000 appears to be the optimum for spinning). Polyurethanes with a molecular weight higher than 14,000, which were made without special care, are already slightly reticulated and therefore only moderately orientable. (It appears that to a low degree also two urethane groups from different chains with an excess of diisocyanate can react with each other, forming complex polyureas.)

The standard polyurethane from 1,6-hexane diisocyanate + 1,4 butylene glycol is on the market in the form of fibers as Perlon U⁸). (Footnote 8: Compare the excellent treatise by H. Stadlinger, Chemiker Zeitung 67, 171, (1943) and for plastics, as Igamid U⁹) (Footnote 9: German tradenames Nylon (6/6) Perlon-T and Igamid A resp., polycaprolactam—Perlon L and Igamid B resp.)

It is surprising that the polyadic acid-hexamethyl diamide, the polycaprolactam and the polyurethane possess an average molecular weight of 8-15,000, if produced in a normal manner, which means with relatively short chains, from which a resin rather than a thermoplastic with unusually high qualities of resistance could be expected. These compounds are in fact less valuable in an unoriented state and acquire valuable properties only after an extensive parallel orientation of their chains (oriented fiber).

Due to its milder production process Perlon U is more uniform in regard to the polymerization than Nylon and polycaprolactam. The distribution of the polymer homologous in the "fusion" and "solvent" polyurethane is considerably different¹⁰).

(Footnote 10: A process of the I.G. Hoechst, pat. appl. I. 68699 of 1.41 and several supplements, permits producing polyurethane through a condensation process, for example, from Cl.CO.O.(CH₂)₄.O.CO.Cl + NH₂.(CH₂)₆.NH₂. By this method a very soft "Perlon U" is obtained which is less uniformly polymerized and consequently possesses a wider thermoplastic range.)

Perlon U has many properties in common with the polyamides but besides that, and owing to the peculiar urethane grouping, which is neither an ester nor an amido group, it has

certain characteristics which create a partly valuable, but in many respects also an unfavorable, effect in the practical application and processing of the new synthetic.

Perlon U has the sharpest but also the lowest (m.-p. = 183°, about the same as acetate silk) melting point of the three most important superpolymers which can be spun which is undesirable for a number of applications. Its softening point (Vicat-degree) is around 170°C. which is still 10 degrees higher than for the purely thermoplastic polycaprolactam (softening point ~ 160°, melting point = 212°C.).

Thermally, the polyurethanes are not too stable. Above 220°C. they disintegrate, especially in the presence of metals, partially into their components (evidently equilibria). It is impossible, therefore, to process polyurethanes with a melting point above 230°C.

The great difference between unoriented Perlon U (spec. gr. 1.18) and oriented Perlon U (spec. gr. 1.21) is remarkable. Polyurethane has such a strong tendency to crystallize that special precautions have to be applied when Perlon U silk is stretched.

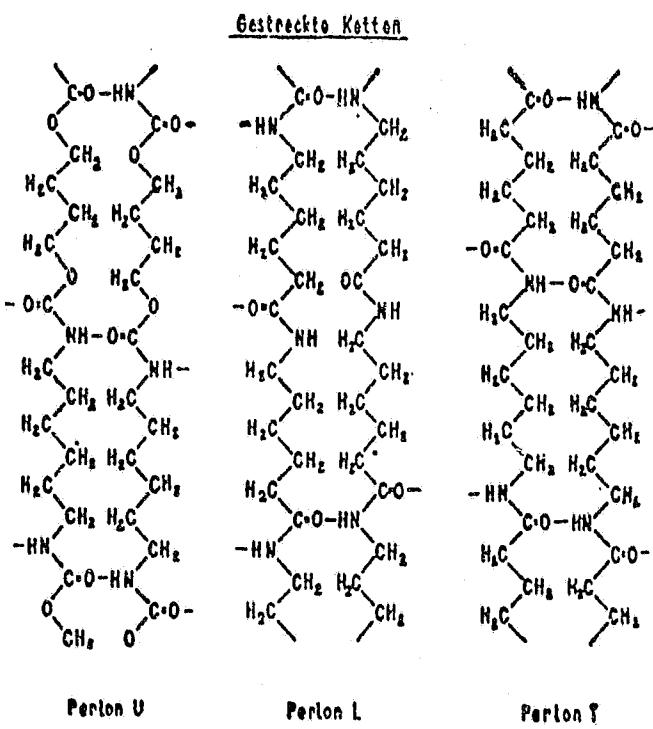


Fig. 2.

From this juxtaposition it becomes evident why the orientation of the polycaprolactam chains (Perlon L) proceeds so easily because only every second amide group can put its H-linkage into operation (besides the softening effect of the content of lower polymer homologues). In the polyurethane (Perlon U) however, each H-atom finds its counterpart, exactly as with Nylon. The higher specific gravity points to an especially good adaptation ability of the polyurethane chains into the crystal lattice, leading to the conjecture that perhaps an additional valency action between $>\text{CH}_2\cdots\text{O}<$ has something to do with it.

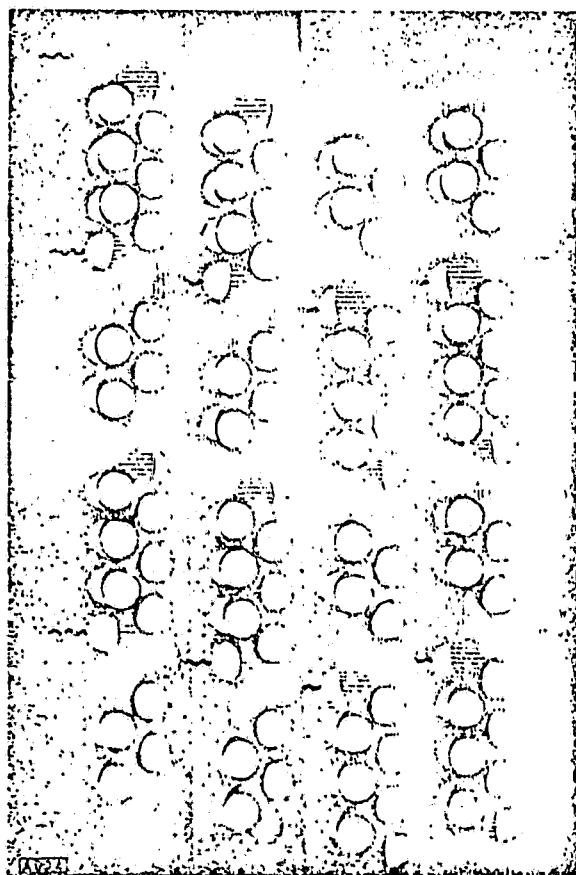


Fig. 3.

Polyurethane chains in an ideal orientation
(Stuart's atom-models)

The polyurethane molecule which can be spun has a chain length 25 times as great as the cut shown above.

From these statements one could have expected the qualities of resistance of the most extensively oriented fibers from polyurethane to be higher than the ones from the two super-polyamides. So far, however, the polyurethane could be processed into fibers with practically the same properties of resistance. With Perlon U, top values of resistance up to 8 g./den. were obtained in the laboratory. (Natural silk = 3.5 g./den., commercial Nylon \sim 5.3 g./den.)

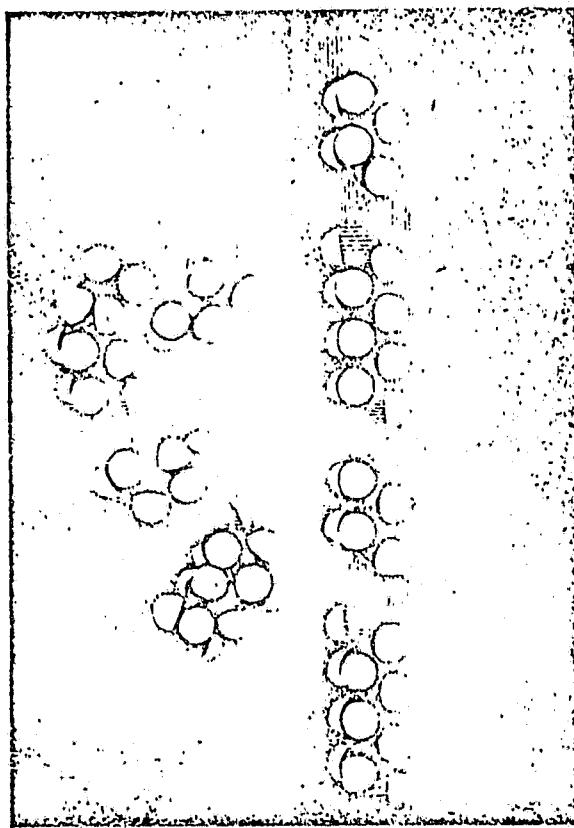


Fig. 4.

Polyurethane Chains

Unoriented and convoluted
and stretched to a maximum form.

The low tendency to absorb water of Igamid U and all the other polyurethanes is especially characteristic.

720a

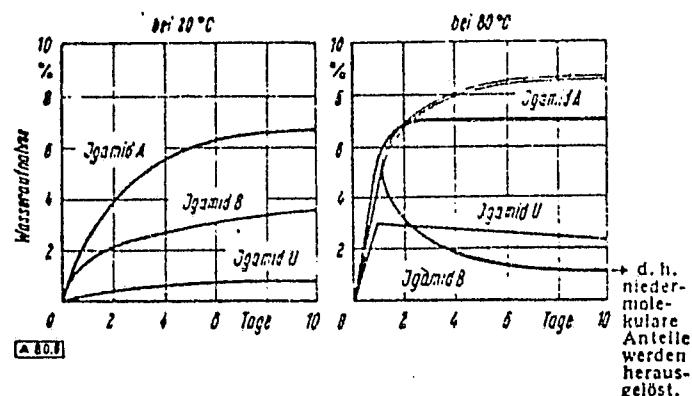


Fig. 5.

Water absorption of the Igamids (ejected pieces)

On the side of above diagram, "at 80°C." means parts of a lower molecular weight are dissolved out.

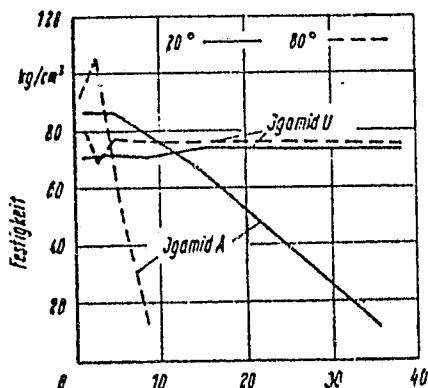


Fig. 6.

Storing in Days
Performance of Igamids in HCl 5%

Though with a rising number of CH_2 - groups in the polyurethane chain (at about the same molecular weight), the water absorption decreases further. The resistance values as well as the melting points decrease because the molecule becomes more and more similar to a paraffin.

As for electric qualities and especially in weather-proofness, the polyurethanes are superior to the poly-

amides and are also considerably more acid-proof.

These specific properties in combination with the other good properties of the superpolyamides (polyurethane), contribute to make the Igamid U an outstanding high melting thermoplastic, also in the field of plastics.¹¹⁾ (Footnote 11: Pabst: Kunststoffhandbuch, 7. ed. 1942, p. 111 and brochures of I.G.: "Igamid U.") Its processing in die casting is already much simpler than that of the polyamides. It does not need a preliminary drying. The Igamid U made by the fusion process does not become brown if melted again on the air and the die casting moldings keep their measurements. It can also be press-molded. The other properties as shock-bending strength, tensile strength, resistance to cold, are practically the same as of the polyamides.

	Igamid U	Igamid A	Igamid B
Spez. Gewicht	1,21	1,14	1,15
Fp. ca.	183°	255°	210°
Spritzkörper			
Brinell-Härte bei 60° (kg/cm²)	750	1000	600
Vicat-Grad	170—180°	220—225°	160—180°
Schlagbiegefestigkeit (cm"/kg/cm²)	ca. 100	über 100	—
Preßkörper			
nicht orientierte Platten			
Zerreißfestigkeit (kg/cm²)	620	—	380
Kältebeständigkeit	+ 8°	—	+ 13°
orientierte Platten			
Zerreißfestigkeit (kg/cm²)	längs 1874 quer 1100	—	1050 860
Zerreißeindruck (%)	längs 60 quer 81	—	73 70
Kältebeständigkeit	-30	—	-30

Table 1.

Schlagbiegefestigkeit - shock-bending strength; Zerreißfestigkeit - tensile strength; Zerreißeindruck - extensibility to breaking point.

In the field of fibers Perlon U is especially interesting for the manufacture of bristles. These bristles are considerably harder and with their stiffness much less sensitive to moisture than Nylon (6/6 and 10/6) and the especially soft caprolactam bristles. The polyurethane is also very suitable as a substitute for horsehair.

The stiffness of Perlon U fiber is especially suitable for its application in cellwool-mixed textiles. The low

permanent extension (extension to breaking = 9%) and high acid-proofness of the new material will make it suitable for normal application, especially for the technical use in the manufacture of highly stable cable insulations, driving belts, fishing implements, acid-proof filter cloth, sieves, coverings, etc.

In the dyeing process Perlon U differs from the super-polyamides. Not having any basic groups it cannot be dyed with acid dyestuffs like the polyamides, but only with dyes for acetate silk and partially also with dye-stuffs soluble in fat.

The polyurethanes which are produced from a uniform di-isocyanate and a uniform glycol (without side chains), are cold soluble only in formic acid, H₂SO₄, cresol and best in phenol water (90:10) mixtures. (The viscosimetric measurements are suitably performed in m-cresol)¹² (Footnote 12)(The viscosimetric constant Kaeger in m-cresol is 1.34×10^{-4} according to author's measuring.)

From ethylene glycol no serviceable polyurethanes can be made because they decompose with development of gas when melted. Upwards from 1,3-propylene glycol, all primary diols are suitable.

Secondary hydroxy groups mostly produce polyurethanes with too low a melting point which are strongly thermoplastic and thermically not stable enough. They are not suitable for the manufacture of fibers. The other polyurethanes with side chains are likewise not serviceable because the latter strongly increase the solubility in organic solvents and decrease the strength qualities on account of the wider distance of the chains. Glycols with tertiary OH groups are also not suitable for the formation of polyurethane because their urethanes mostly decompose at about 170°C., splitting off CO₂.

Translation of words in Column 4, headed "Properties", as shown in following Table 2:

sehr gut fadenziehend - very easily forming threads

hornartig - hornlike

sprode - brittle

zersetzt - decomposing

Faden elastisch abgleitend - thread gliding off elastic

streckbar - extensible or stretchable.

Dilisocyanat	Glykol	Fp.	Eigenschaften
- $(CH_2)_6-$	1,4-Butandiol	193°	
"	1,6-Hexandiol	180°	
- $(CH_2)_8-$	1,10-Dekandiol	171°	
- $(CH_2)_6-$	1,4-Butandiol	159°	
"	1,3-Propandiol	167°	
"	1,5-Pentandiol	151°	
"	1,9-Nonandiol	147°	
"	$OH-CH_2-CH_2-O-CH_2-CH_2-OH$	120°	
"	$OH-(CH_2)_3-O-(CH_2)_3-OH$	124°	
"	$CH_2-CH_2-CH_2-CH_2-CH_2-CH_2$	104°	
	$\begin{array}{c} OH \quad OH \\ \quad \\ OH(CH_2)_3-\text{C}_6\text{H}_4-(CH_2)_3-OH \end{array}$	158°	sehr gut fadenziehend
	$\begin{array}{c} OH-(CH_2)_3-S-(CH_2)_3-OH \\ OH-(CH_2)_3-S-(CH_2)_3-OH \end{array}$	129—134°	
- $(CH_2)_6-$	1,4-Butandiol	160°	
"	1,3-Butandiol	77—82°	hornartig
"	1,6-Hexandiol	153°	sehr gut fadenziehend
"	$\begin{array}{c} OH-\text{C}_6\text{H}_4-OH \quad \text{cis} \\ \text{trans} \end{array}$	215—220°	gut fadenziehend, spröde
"	$\begin{array}{c} OH-\text{C}_6\text{H}_4-OH \quad \text{trans} \\ \text{trans} \end{array}$	250—255°	zersetzt sich
"	$\begin{array}{c} OH-CH_2-\text{C}_6\text{H}_4-CH_2-OH \\ OH-(CH_2)_3-O-\text{C}_6\text{H}_4-O(CH_2)_3-OH \end{array}$	168°	schlecht fadenziehend
	$\begin{array}{c} OH-(CH_2)_3-O-\text{C}_6\text{H}_4-O(CH_2)_3-OH \end{array}$	208—212°	Faden elastisch abgleitend
- $(CH_2)_6-$	1,4-Butandiol	136—140°	sehr gut fadenziehend
- $(CH_2)_8-$	1,5-Pentandiol	143—146°	
"	1,4-Butandiol	121—123°	
- $(CH_2)_6-$	1,12-Dodekandiol	~260°	zersetzt sich
	1,10-Dekandiol	215—219°	sehr gut fadenziehend
	1,4-Butandiol	126—133°	fadenbildend, spröde
			gut fadenziehend und streckbar

Table 2.

Properties of several linear polyurethanes

Building benzene rings into the polyurethane produces more brittle and poorly fiber forming compounds. Serviceable fibers are obtained only after the influence of the bulky nuclei is compensated by an increase of CH_2 groups, such as:



The polyurethanes from the homologous glycol series with application of the same diisocyanate show the same alternating melting points.

The polyurethanes from glycols with an odd number of CH_2 groups have a lower melting point and are surprisingly much more clear like glass than the vicinal ones built up from even numbers of components.

In its physical phenomena, as for example, in its extensibility up to 4.3 times its original length under orientation of the molecule chains, its permanent deformation under the influence of boiling water and simultaneous strong tension, the Perlon U resembles very much the super-polyamides.

Besides Igamid U and Perlon U respectively, the following types may become of technical importance:

The polyurethane from 1,4-butane diisocyanate + 1,4-butylene glycol: it has the advantage of a 12°C. higher melting point (m.p. 194°C.) and could be manufactured cheaper if the butane diisocyanate could be produced absolutely pure.

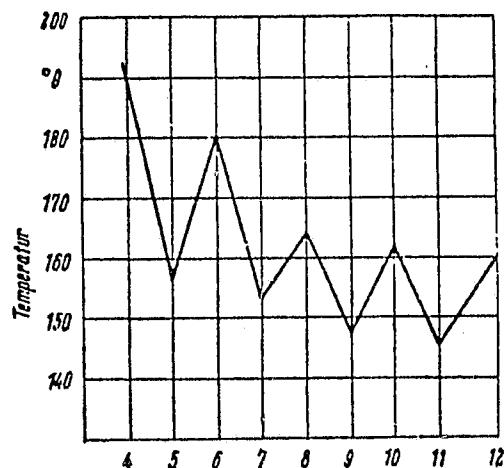
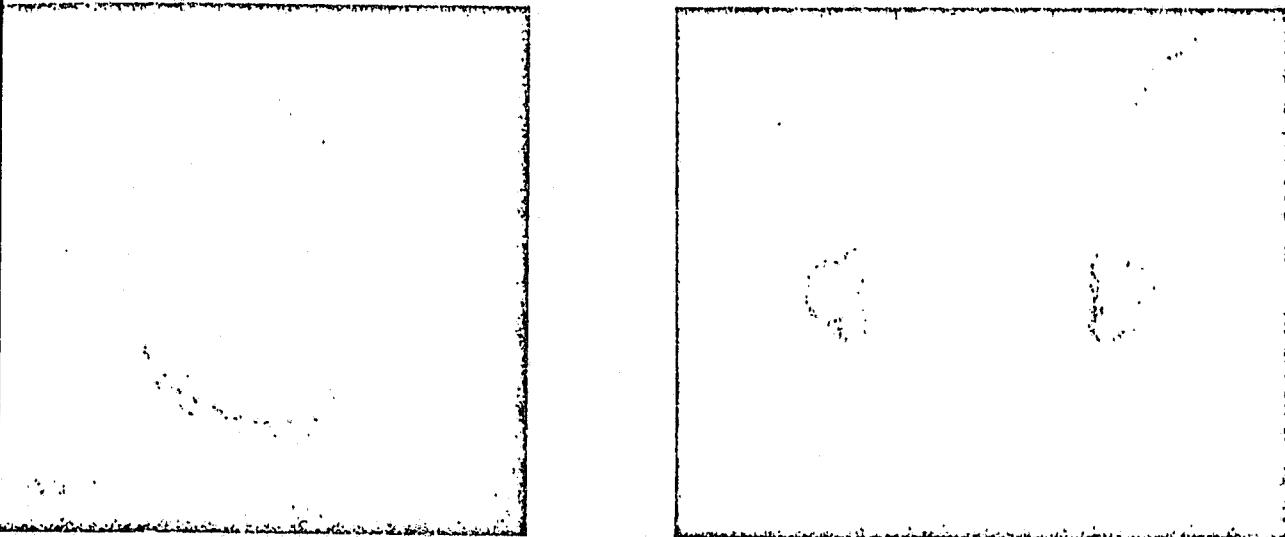


Fig. 7.
Number of C-atoms in Diisocyanate

Explanation: Melting points of polyurethanes from diisocyanates with rising chain length by application of butane diol.



a) in unoriented state

b) in oriented state

Fig. 8

X-ray Diagram of Igamid U

LINEAR MIXED POLYURETHANE

The mixed polyurethane¹³) (Footnote 13: names of cooperators) which can be prepared through application of a mixture of various glycol components and/or diisocyanate components, differ from the uniform polyurethanes in regard to the former's considerably better solubility, for example, in chlorinated hydrocarbons, even in the cold, a lower melting point, a very wide thermoplastic range, greater softness and better compatibility with plasticizers. They are therefore the suitable materials for the manufacture of fibers, foils and leather substitutes.

A polyurethane in which only 10 mol % of the butylene glycol are replaced by methyl-1,6-hexane diol (from the mixture of isomer adipic acids) is more thermoplastic and consequently easier to extrude (eject) than the uniform material. It will be marketed as Igamid UM. In general it is immaterial which glycols are used for addition together with the cheap 1,4-butylene glycol. As a leather substitute, Igamid UL has already been produced on a technical scale from 1 mol of 1,6-hexane

diisocyanate + 1/2 mol of 1,4-butylene glycol + 1/2 mol of methylhexane diol. A mixed polymerizate with quite similar properties was built up from 1/2 mol of 1,4- + 1/2 mol 1,6 diisocyanate + 0.8 mol of 1,4-butylene glycol + 0.2 mol methylhexane diol.

Igamid U is a very soft material, easily soluble in chloroform-methanol mixtures up to a K-value of about 75. In many of its properties it is superior to Blank-leather.

	ULW 15	ULW 25	6 A ¹⁴⁾ 33% Plasticizer
Tensile strength Kg/cm ³	440	340	250
Extension	400%	400%	250%
Tearing-out strength after puncture Kg/mm	13	10	10
Tearing-out further strength after p. Kg/mm	5.5	4.0	4.5
Stiffness (m kg/cm ²) + 40°C.	3.6	3.6	4.3
+ 20°C.	9.0	5.9	6.0
0°C.	16.9	8.9	9.6
- 20°C.	33.7	23.0	42.4
Resistance to cold (Knock in the cold)	-25°C	-25---30°	-25°

Table 3.

Average values for Igamid ULW 15, ULW 25
and 6A.

(Footnote 14: Igamid 6A is a mixed condensate from caprolactam and adipic acid-hexamethylene diamide.)

The brands Igamid ULW 15 and 25 contain 15 and 25% respectively, plasticizer (mixture of benzene-sulfomethyl and butyl amide = Dellatol).

The manufacture of the mixed polyurethanes is very simple. In a heatable kneading machine the glycol mixture is charged first and the diisocyanate is added until a highly tough melt with a K-value of about 100 is formed. A small addition of anti-oxidants is advantageous. Shortly before the final consistency is reached, it is

suitable to add the corresponding amounts of plasticizers or fillers. The still hot, completely colorless mass is pulled through a calender and sold as "crude skin".

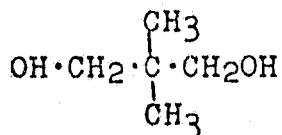
These higher molecular UL types are doubtless already slightly reticulated but, in spite of this, can still be calendered under an increase of their strength properties.

The mixed polyurethanes with K-values of 90-100, represent the optimum for leather substitutes; their molecular weights are much higher than the ones of mixed polyamides. Such large molecules in the polyamide series can only be obtained by after-treatment with formaldehyde¹⁵⁾ or diisocyanates¹⁶⁾. (Footnote 15: DuPont Am. Pat 2,177,637 of Sept. 1938); (Footnote 16: D. R. Pat. 750,427, I.G.-Lu./Le of Jan. 1942).

The polyurethane-leathers are superior to the Igamid 6 A-leathers (not after-treated with diisocyanate) as far as tensile strength, softness and, above all, insensitiveness against extreme dryness and the so-called shortness, caused by storing in warm water, is concerned.

The resistance against cold also of the UL types is only about -25 to -28°C., which is not yet completely satisfactory for all purposes. Orientation of the leather material will cause a slight improvement of the resistance to cold. A disadvantage of all polyurethane and polyamide leathers is their low filling capacity, more than 10% filler causes a great decrease of the mechanical values.

Valuable types can also be worked out by application of other glycols as, for example, thio diglycol, 1,5-pentane diol, linear polyesters from aliphatic dicarboxylic acids + glycols with OH groups in end position. So far the most cold resisting mixed urethane, with simultaneous preservation of the other good properties, was obtained through simultaneous application of OH-(CH₂)₄-O-(CH₂)₄-OH (from tetrahydrofurfuran). Mixed polyurethanes containing more than 3 components, especially -

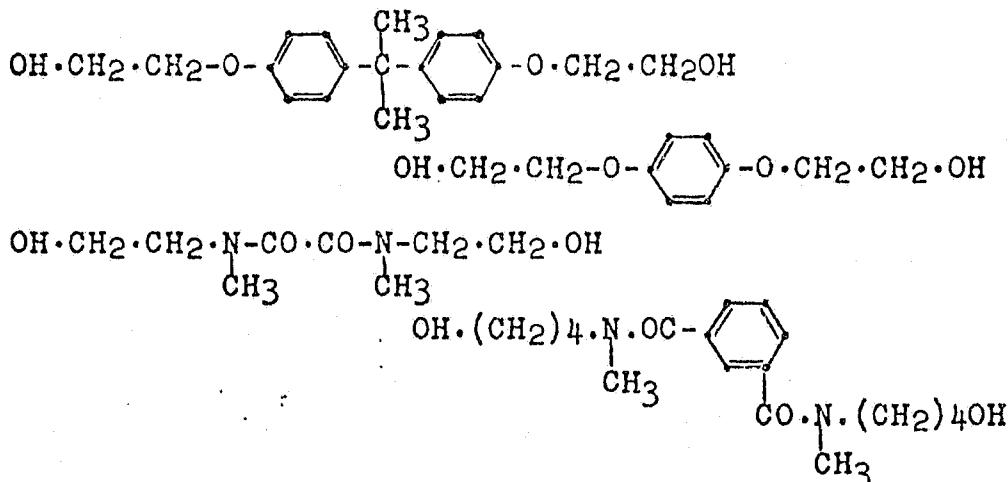


show in many cases decided caoutchouc-elastic properties

in the temperature range of between 10° and about 60°C.

It can generally be stated that the more components used for the building up of mixed polyurethanes, the less uniform their structure becomes and their strength values will decrease.

A simultaneous application of aromatic and too "rigid" components, as, for example



or of aromatic diisocyanates causes a decrease of the resistance to cold.

It seems to be quite unlikely that the more brittle polyurethane foils (lower shock resistance) can successfully compete with the excellent Lyafol-foil in the field of foils and films (Lyafol = calendered polycaprolactam). The mixed polyurethane from:

0.8 mols hexane diisocyanate	0.5 mol 1,4 butylene glycol
0.2 mols $\text{C}_6\text{H}_5 \text{CH}_2 \text{CH}_2 \text{N}=\text{C}=0$	0.5 mol methyl 1,6 hexane diol
$\text{O}=\text{C}=\text{N}$	

represents a film forming material which is especially impermeable for several substances.

It is impossible to specify in the scope of this survey the numerous processing and application processes of the polyurethanes. Mention may be made only of the large number of difficult and new problems which emerged, as, for example, the preparation of polyurethanes with definite K-values, stabilizing the material in the melt against progressing polymerization.

and decomposition, the difficulties in calendering, the production of the diisocyanates and others.

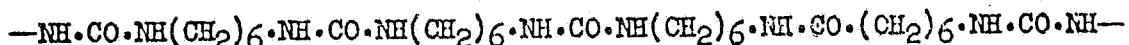
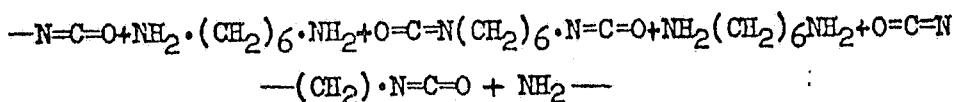
PATENT SITUATION

I.G. is completely independent from the duPont polyamide patents in the field of production of polyurethanes and their application for foils and plastics. In cooperation with the I.G. works, Dormagen and Wolfen processing methods for the application of polyurethanes to silk and bristles have been worked out which are independent from other patents.

The patent situation in the U.S.A. was not clear up to the start of the war. DuPont has also worked in the field of diisocyanates and since then currently taken out patents after this firm was notified as early as 1938 of the I.G.'s research.¹⁷⁾ (Footnote 17: DuPont Ser. No. 275,539 of May 1939 = German applic. I. 68130 of October 1940.) After the war DuPont put diisocyanates on the market also.¹⁸⁾ (Footnote 18: See Chemical Engineering News Edit. Nov. 1946, p. 3098-99.)

POLYUREAS

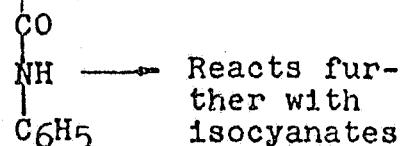
In a reaction, analogous to the polyurethanes, aliphatic, primary diamines with long chains were converted with aliphatic diisocyanates. The expected linear polyureas:



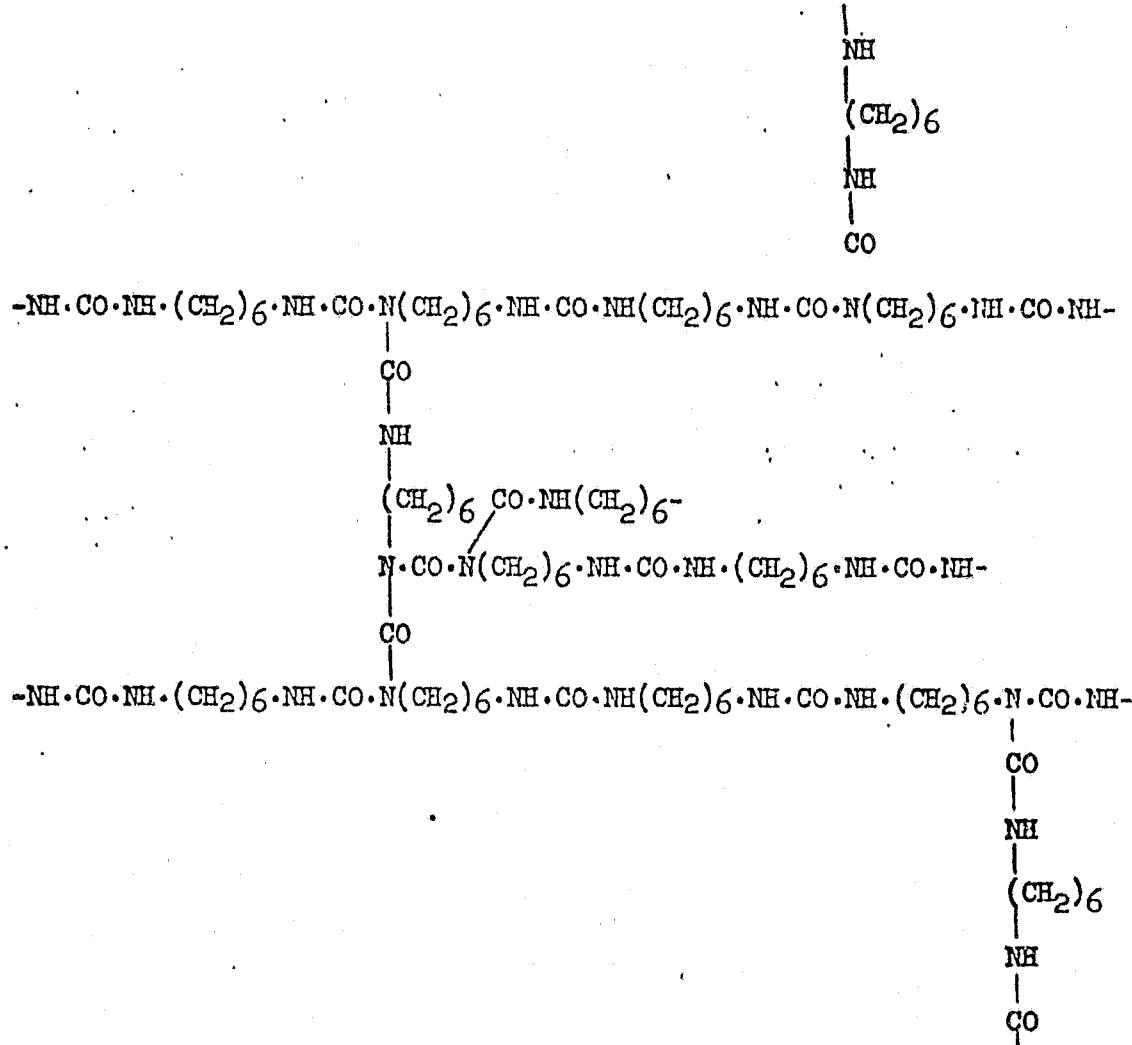
were not obtained, however; but mostly only infusible and hydrophilic polymers which cannot be processed in the melting-spinning process and are therefore practically worthless for the other applications in the plastics field.

In the course of this work, it became evident¹⁹⁾ (Footnote 19: Nordt and Delfs, pat. appl. 77604 - with a molecule of urea as a starter or one mol H₂O+any amount of mol. of mono isocyanates, strongly ramified polyureas can be made. Lieser and Gehlen, Lieb, Ann. Chem. 556, 127 (1944), who describe the preparation of linear polyureas from the diazides, which are converted in an intermediary reaction

into diisocyanates, have overlooked this observation) that the urea group as such can react with isocyanates under formation of biuret-like compounds, for example,



and that consequently from diamines or H_2O + diisocyanates, never the linear but always only strongly reticulated polyureas are formed.



On the other hand, from glycols with simultaneous application of di-secondary aliphatic diamines 20) (Footnote 20: I. 72830 of 7.42. W. Lehmann, O. Bayer, H. Rinke), for

example, diisopropyl 1,6-hexamidine or $\text{RNH} \cdot (\text{CH}_2)_n \cdot \text{OH}$, through the solvent method, thermoplastic, viz. extensively linear polyurea mixtures are obtained which is obviously and first of all due to steric reasons (wider distance of the polyurea chains). But also these become insoluble after a while. From diisocyanates + hydrazine, however, serviceable fibers are said to be obtained²¹⁾ (Footnote 21: I. 74534 of 3.43. M. Wohlraff (I.G.Dormagen) and later also the Phrix concern.)

RETICULATED POLYURETHANE

Desmophen-Desmodur Lacquers

The linear constructed polyurethanes are practically all thermoplasts, which means that they can be molded and processed in the heat or with solvents and plasticizers respectively. If, however, diisocyanates are reacted upon compounds with more than two reactive H-atoms, such as glycerine, acetylcellulose, polyesters with free hydroxy groups, polyvinyl alcohol, etc., tridimensional macromolecules are formed which are insoluble in all organic solvents as well as infusible. Their application for plastics is therefore very limited. (Casting resins workable only with shaving tools.) If, therefore, these compounds are to be practically utilized, the addition of diisocyanates to polyoxy compounds has to be accomplished in the finishing process. In the fields of lacquers and molding compounds, the two components have to be brought to reaction either on the object to be coated or in molding through heat and pressure²²⁾ (Footnote 22: D.R.P. 756058 of 3.1940 = Fr. Pat. 876285 and numerous additional applications).

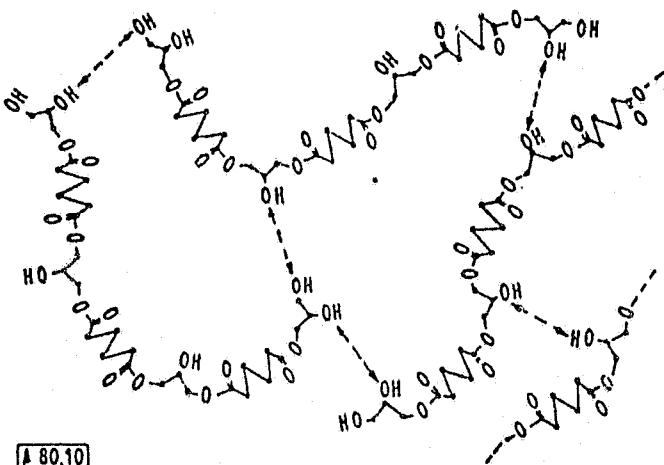


Fig. 9

Reticulation Scheme of Desmophen-Desmodur²³⁾

Footnote 23: Desmophen = trade name for the polyoxy compounds. Desmodur = trade name for the diisocyanates).

The reticulation scheme of Desmophen-Desmodur gives a very clear picture of the extraordinary extent of variations of the new poly addition process.

For example, an isocyanate-lacquer is prepared through dissolving of a suitable polyalcohol and a diisocyanate in a proportion of about 4:3 of the OH and isocyanate groups in a solvent which is free from hydroxy groups, eventually with addition of pigments. Such a lacquer solution is sprayed on and either left at room temperature or annealed at temperatures up to 160°C. Thus, a completely insoluble and infusible lacquer coating is formed, the capability of resistance to chemicals, elasticity and hardness of which can be varied by application of either preponderantly aliphatic or aromatic components²⁴⁾ (Footnote 24: names of cooperators).

For this method it is, of course, self-evident that the components do not react with each other prematurely and at ordinary temperatures because the lacquer solutions would otherwise gelatinize. Several slowly reacting diisocyanates are quite satisfactory in this respect. Depending on the conditions and on the starting materials, these freshly made solutions are stable for many hours and even days, especially if catalysts, as organic bases, alkali, heavy metal salts, and water are carefully excluded.

Further observation disclosed that compounds with ether groups, such as cellulose derivatives, will retard the poly addition. Other stabilizers are Azo dyes which are soluble in organic solvents and certain compounds with an acid reaction as thioureas, cyanoacetic acid ester, etc.

Of the far more than 100 diisocyanates prepared in the laboratory, the compounds as shown in Table 4 are serviceable and can technically be produced.

For determination of the equivalents the "isocyanate number" was introduced which indicates the grams of N-C=O groups contained in 100 g. substance. This determination is made with a 1-n-diisobutylamine solution in chlorobenzene. The not reacted amine is return titrated with HCl. (G. Spiegelberger.)

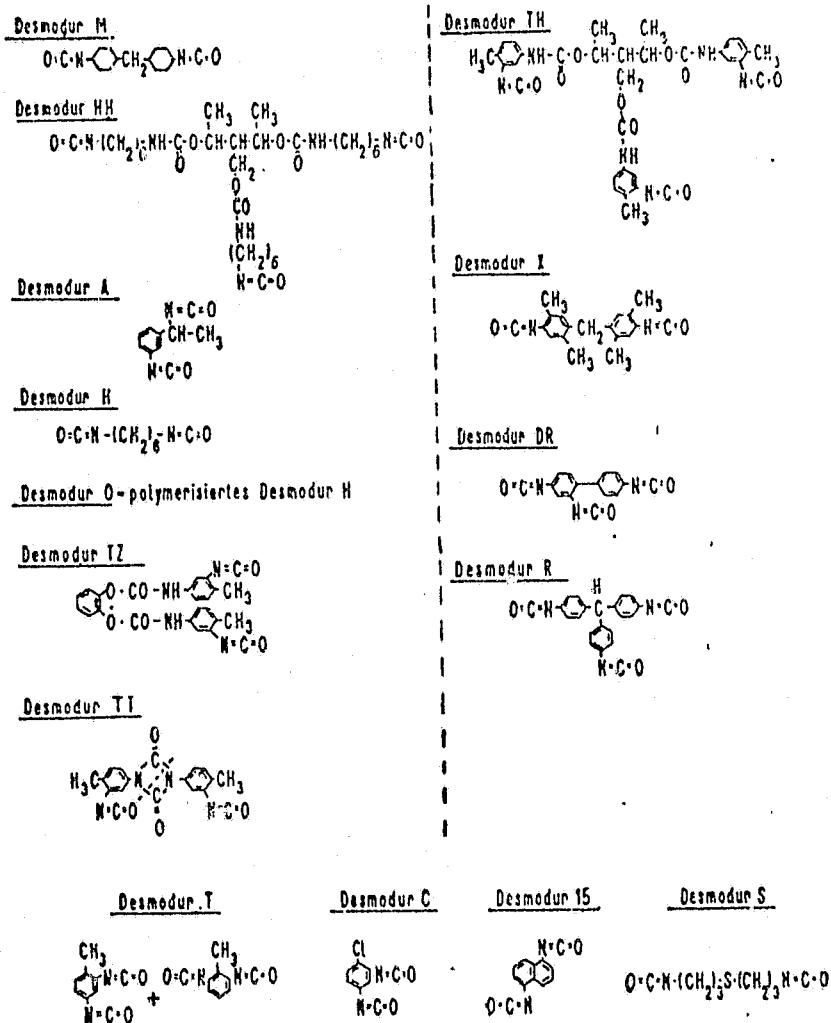


Table 4.

Serviceable and Easy-to-prepare Diisocyanates.

This small selection permits the most varied applications and graduations in the order of the groups to be added.

Desmodur 15 is the most reactive compound, the reactivity decreasing in the following order: 15, C, T, H, X, M, the most inert diisocyanate being S.

It can generally be stated that the isocyanate groups which are bound to aromatic rings are the most reactive ones. The presence of negative substituents increases the reactivity still more. Aliphatic isocyanates (on the primary C) are considerably more inert,

the reactivity of the isocyanate group on the secondary C-atom is still more limited (cyclohexyl) and the most inert ones (not regarding the adhering C-atom) are those which contain the ether or sulfide bridges in their molecule. Consequently the reactivity of the two isocyanate groups in Desmodur A and the diisocyanate from hexahydrobenzidine is very different. In tolylene 2,4-diisocyanate also, the isocyanate group in 4-position is much more reactive than the sterically hindered group in ortho position.

As an interpolation it may be mentioned here that all compounds with H-atoms, replaceable by alkali metal, can be added to isocyanate groups. By far the most reactive group is the primary NH₂ group, so much so that the reaction with isocyanate can be accomplished in aqueous solutions or emulsions with a practically quantitative yield. The next ones in order are: H₂O, alcohols, carboxylic acids, the urea grouping, phenols, active methylene groups - in other words, beginning with the alcohols, all isocyanate reactions have to be absolutely free of water.

Further reactive groups are: mercapto, carbon amide, and sulfur amide groups. Furthermore, the oximes, formaldehyde and HCN are included.

Diisocyanates with a relatively high vapor pressure as H and T are physiologically very disagreeable substances because they are tear-exciting²⁵), (Footnote 25: See report of Industrial Hygiene Laboratory, Prof. Gross, I.G.-Leverkusen) and cause asthmatic troubles with many persons, but without permanent consequences.²⁶) (Footnote 26: Small amounts of NH₃ in the air destroy the evaporated diisocyanates immediately). For these reasons, the completely odorless and physiologically unobjectionable Desmodurs TH, HH, TZ and TT were produced.

The technically most important TH is made through addition of 3 mols of tolylene diisocyanate to 1 mol of hexanetriol²⁷), (Footnote 27: Pat. appl. I. 72821 of 7.24.1942) representing a colophony-like resin without vapor pressure, easily soluble in acetic acid ether.

Polyesters with oxy groups have proved to be especially valuable in the series of compounds containing oxy groups. The following types are on the market:

	<u>Combination With Desmodur</u>
Desmophen 1200 = polyester from 3 mol of adipic acid + [1 mol triol (triol = glycerin, hexane triol, trimethylol propane, etc.) 3 mol butylene glycol	Highly elastic
Desmophen 1100 = polyester from 13 mol of adipic acid + [2 mol triol 3 mol butylene glycol	
Desmophen 900 = polyester from 13 mol of adipic acid + 4 mol triol	
Desmophen 800 = polyester from 2.5 mol adipic acid + 0.5 mol phthalic acid + 4 mol triol	
Desmophen 300 = condensation product from 1 part Desmophen 900 + 1 part xylene-formaldehyde resin.	
Desmophen 200 = polyester from 1.5 mol adipic acid + 1.5 mol phthalic acid + 4 mol triol	very hard

Table 5.
Compilation of the Most Important Desmophens

OH-number is between 130-125, viz. 4-10 g.OH in 100 g. substance.

The Desmophens with low numbers produce hard coatings and the ones with the highest figures produce soft and partially even caoutchouc elastic coatings. It can generally be stated that a lesser reticulation and the application of purely linear initial materials produces highly elastic and soft polyurethane, and that on the other hand, a stronger reticulation and/or the application of rigid,

essentially aromatic components, produces hard to brittle tridimensional polyurethanes.

Of the enormous number of polyoxy compounds which can be cheaply produced, the following have proved to be especially valuable: OH groups containing mixed polymerizes of a lower viscosity, as for example, a saponified copolymerize from 80% vinyl chloride + 20% vinyl acetate of a K-value about 30; acrylic acid-butyl ester + vinyl chloride copolymerize partially converted with $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$; glyptal resins; alkydols; ricinoleic acid-polyester; OH groups containing phenolic resin as the Luppen, benzyl-cellulose, Cellit; condensation products from polyester + xylene-formaldehyde resins containing much oxygen.

The Desmophens and Desmodurs are applied in acetic ester solution or in mixtures with aromatic substances²⁸⁾, a lacquer mixture:

(Footnote 28:

40 parts Desmophen 1100 20 parts acetic ester 20 parts butyl acetate 20 parts toluene	are mixed with 90 p. Desmodur TH in ethyl acetate-toluene sol- ution 50%.
--	--

The lacquer is dry after about 3 hours and completely hardened after 4-5 days.)

The addition reaction takes place on the coated object either at ordinary temperature or through heating up to 150°C., the annealed lacquers generally showing somewhat better properties. It is an established fact that it is possible to thus produce lacquers with properties which were unknown up to now.

On the strength of thoroughgoing tests over several years they show the following advantages:

1. Unlike the alkydol lacquers, they can be coated on at considerably lower temperatures, partially even at room temperature and can therefore be applied to heat-sensitive materials as paper, textiles, leather, wood, rubber articles, plastics, etc., producing a lacquer coating of a quality which could not be achieved so far.
2. The possibilities of variation of their qualities, for example, elasticity, is such as cannot be reached by other lacquers.

3. They are distinguished by an unusual firmness of attachment on the base and by a very high lustre, density of pores and, therewith, impermeability for gases. In most cases they possess a high resistance to cold (-40 to -60°). Their fastness to water is excellent (25-50% of the swelling of high grade lacquers) as is also their binding capacity for pigments, weather proofness and resistance to solvents and alkalies (that is, resistant to hot tricresyl phosphate, chlorinated hydrocarbons).

4. Their body volume is very high (saving of manipulations and solvents).

5. Due to the reactivity of all movable H-atoms in the diisocyanate groups, which regulate the electric conductivity, the diisocyanate lacquers have a high electric resistance (spec. resist: $10^{-15} \cdot 10^{-16}$ ohms x cm) and also an extraordinary creep-current resistance, of great importance for the manufacture of cable lacquers and electro-insulating papers.

Disadvantages of the new lacquering process:

1. Low stability of the finished lacquer solutions which have to be used in one day.

2. The use of solvents which are free of hydroxy groups of which there is not much to select from, also the complete exclusion of water.

3. The physiologically disagreeable effect of the lower molecular diisocyanate.

4. Difficulties in cleaning vessels, spraying pistols and brushes.

5. The sometimes higher price of the new products.

During the years 1942-44 up to 40 tons per month of Desmophen-Desmodur (T) were produced. They were applied principally as adhesive compounds, as corrosion resistant coatings on light metals, as lacquers for wooden parts exposed to the influence of the weather, for weather-proofing of cloths, acid-proofing of lumber, impregnation of armature windings, of cardboard and metal meshes which produce such high grade packings against water, alcohol, oil, boiling chlorobenzene, and even phenol.

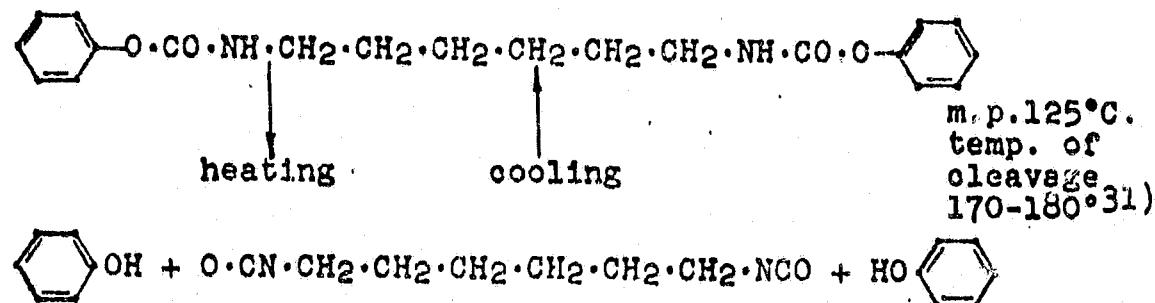
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Due to the unsurpassed resistance against Lost (poison gas) of the Desmodur-Desmophen combinations, the manufacture of 100,000 protective covers against gas from crepe paper + Desmophen 1100 + 1200 T was ordered.

Large possibilities for future application suggest uses such as coatings for ships, protection of apparatus, patent leather, compound glass and especially for electrotechnical purposes and finishings and dressings for textiles.

Cleavage Agents for Isocyanates (Disguised Isocyanates)²⁹
(Footnote 29: Names of cooperators)

The great reactivity of the isocyanate group and its decomposability through H₂O suggested very early the problem of their stabilization. It was known, for instance, that phenylurethanes are split through heat into isocyanates + phenol and that obviously an equilibrium of temperatures exists. It should be possible to shift this equilibrium in favor of the decomposition if compounds are present which render more stable addition products with the isocyanate group, for example, aliphatic amines or alcohols. In fact, this idea could be realized in the most varied manner by finding addition groups which could be relatively easily split off (disguised isocyanates or "isocyanate splitters")³⁰



Action of "Disguised" Diisocyanates

(Footnote 30: The action as a splitter of a diisocyanate can easily be tested. This compound is dissolved together with sec. cellulose acetate, spread on glass and the temperature determined at which the cellulose film has become insoluble.)

(Footnote 31: I. 64524 of May, 1939, P. Schlack (Lichtenberg)).

anates made it possible to catch, as an intermediary product, a carboxylic acid-carbamic acid anhydride which splits off CO₂ when heated, forming the amide 2CH₃COOH + HOCN·(CH₂)₆NCO → CH₃·CO·O·CO·N(CH₂)₆·NHCO·O·CO·CH₃ (m.p.

67°C.) → CH₃·CO·NH(CH₂)₆·NH·CO·CH₃ + 2CO₂ (S. Petersen). This reaction is, however, quite often very complex, depending on the isocyanate used. If phenyl- and especially p-nitrophenyl isocyanate is applied up to 70% acid, anhydrides are formed and also diphenyl ureas + CO₂. See the exhaustive work and voluminous citations in the literature. C. Naegeli and A. Tyabji, Helv. chim. Acta 17, 931 (1934); 18, 142, 1935.)

This reaction can be utilized for production of new and highly stable foam-substances. By mixing a polyester from a dicarboxylic acid and a trivalent alcohol still containing free hydroxy- and also carboxylic groups 52), (Footnote 52: I. 69394 of April 1941, Hoechtl and W. Droste; several additional applications), with a diisocyanate in the honey-like mass, addition to the OH groups takes place under a strongly exothermal reaction, whereby at first urethane bridges are formed and subsequently carboxylamide bridges through reaction with the COOH groups and simultaneous cleavage of CO₂.

The mass, which becomes tougher and tougher, swells up like a dough and hardens more and more under the progressing enlargement and reticulation of the molecule. The material, which at first can still be molded at 100°C. hardens completely through subsequent heating eventually into a final shape. Thus, it is possible to manufacture foam compounds with very high properties of strength such as were not known so far, and with any desired degree of elasticity through casting in molds.

These foams are sold under the designation "Moltoprens" and consist of:

Desmophen 900S - polyester from 3 mols of adipic acid
+ 4 mols of triol

Desmophen 1200S - polyester from 3 mols of adipic acid
+ 3 mols of butylene glycol
+ 1 mol of triol

both having an acid number of about 30 and an OH number of 300 to 350 (ca. 10% OH groups).

PLAINTIFF'S EXHIBIT 9

U. S. Patent No. 2,726,219, Frederick B. Hill, Jr.

Pages 740a to 741a

United States Patent Office

2,726,219

Patented Dec. 6, 1955

1

2,726,219

POLYALKYLENE ETHER GLYCOL-ARYLENE DIISOCYANATE ELASTOMER SPONGE AND PROCESS FOR PREPARING SAME

Frederick B. Hill, Jr., New Castle, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application August 24, 1951,
Serial No. 243,575

4 Claims. (Cl. 260—2.5)

This invention relates to the preparation of new and valuable elastomeric sponge material and to a method for preparing the same from polyalkylene ether glycols and arylene diisocyanates.

In general, the manufacture of elastomeric sponge material from elastomers of various types is produced by expanding the elastomeric material in an uncured state with various types of so-called "blowing agents" and then effecting a curing or vulcanization of the elastomer in the blown condition. Two types of sponge materials are produced depending upon the processes involved, namely, those known as the continuous or open cell sponge, and the closed cell sponge. In the latter type the cells, or at least the majority of them, are closed, that is, not connected with one another, so that they are not water absorbent like the open or continuous cell sponge.

Usually the elastomeric sponge material is blown by the use of inorganic blowing agents such as sodium bicarbonate or by various organic blowing agents, although the introduction of inert gases such as nitrogen or carbon dioxide into the elastomers under high pressure has also been employed to expand vulcanizable elastomeric materials prior to vulcanization. In general, the open cell type sponge lacks structural strength and the quality of absorbing shock to a much greater degree than the closed cell types, and the purposes for which the two types are used are generally quite different. In the use of inorganic blowing agents the salts employed, which are electrolytes, are retained to some extent in the sponge material, and in the use of the organic blowing agents, which have found particular use in the production of closed cell sponge, the organic residues are likewise retained in the resulting products.

In my co-pending application Serial No. 237,660 filed July 19, 1951 (of which the present application is a continuation-in-part), now abandoned, a new type of elastomeric material is described which is produced by the reaction of high molecular weight polyalkylene ether glycols with arylene diisocyanates.

It is an object of the present invention to produce elastomeric sponge material from the new polyalkylene ether glycol-arylene diisocyanate reaction products by a process which requires no additional blowing agent. It is a further object of the invention to produce closed cell elastomeric sponge material which is resilient and tough and which can be cast or formed into articles of varying shape, and to produce articles having a closed cell structure which have a high degree of flame resistance and which are both freeze resistant and heat resistant, giving them utility over a wide range of temperatures.

I have found that, in the production of the elastomeric materials more particularly described in my co-pending application Serial No. 237,660, now abandoned, in which a polyalkylene ether glycol such as the polyethylene ether glycol and the polypropylene ether glycol, which has a molecular weight of from 750 to 6000, is reacted with an arylene diisocyanate and a somewhat larger amount of water is added in the completion of the reaction than that called for in the formation of the polymers them-

2

selves, closed cell sponge-like material can be produced, the expansion being due to the carbon dioxide generated in the final stages of the reaction. These sponge materials, which are of a substantially closed cell structure, are much softer than the rigid plastic foams that are usually produced from polystyrene, and have a high resistance to swelling by aliphatic hydrocarbons and are relatively insoluble in all of the common organic solvents. They are, however, swollen by certain of the aromatic solvents such as the aromatic hydrocarbons and chlorinated aromatic hydrocarbons. The final sponge material varies in color from white to pale yellow-brown, most of the types of polymers, as described in my co-pending application, resulting in a sponge which is cream colored. This sponge material is resilient, tough, and has high shock absorbent qualities.

In the preparation of the sponge material the reaction products of the polyalkylene ether glycol and the arylene diisocyanate of the types generally described in my co-pending application Serial No. 237,660, now abandoned, are produced by stirring the molten polyalkylene ether glycol and the arylene diisocyanate at about 75° C. until the reaction is substantially complete, as indicated by no further increase in viscosity, and then approximately 300 parts of water per 100 parts of the reaction mass are added, the water being at a temperature of from about 0° to 40° C. Under these conditions the carbon dioxide that is formed is trapped inside of the elastomer, forming the closed cell sponge structure. To avoid the formation of a tough, irregular surface the product should be dried at relatively low temperatures, that is, at ordinary room temperatures of from about 20° to 40° C. The rate of drying can be accelerated by reducing the pressure.

The procedure above outlined differs from that employed in the preparation of the elastomer itself in which only from 10 to 50 parts of water per 100 parts of reaction mass are employed and the reaction is carried out under milling conditions under which the carbon dioxide is liberated from the mass, with the resultant production of a hard, rubbery mass or clump.

As illustrated in the following examples, polyalkylene ether glycols of a molecular weight of from 750 to 6000 appear to be suitable for the preparation of these new rubber-like products. When using the polyethylene ether glycol, which is considered as having the general formula: HO—(C₂H₄O)_n—C₂H₅OH, the preferred products of the present invention are obtained from those having a molecular weight of from 4000 to 6000. When using the polypropylene ether glycol which is considered as having the general formula: HO—(C₃H₆O)_n—C₃H₇OH, the preferred compounds of the present invention are made from those having a molecular weight of from 750 to 1200. To produce the rubbery, plastic-like products of this invention in which the polyethylene ether glycol is employed, the amount of the arylene diisocyanate employed will vary depending upon the particular diisocyanate, but it has been found that in general, to produce rubber-like materials of this invention the weight ratio of the diisocyanate to the polyethylene ether glycol will be between 0.25:1 and 0.33:1 provided the molar ratio is between 7.5:1 and 12.0:1. When using the polypropylene ether glycol, the preferred products of this invention are prepared using a weight ratio of diisocyanate to the polypropylene ether glycol of from 0.5:1 and 1:1 provided the molar ratio is between 1.5:1 and 4.5:1.

Any of a wide variety of the arylene diisocyanates may be employed in place of those specifically used to illustrate the invention in the following examples, the common examples of this class being: 2,4-tolylene diisocyanate; meta-phenylene diisocyanate; 4-chloro-1,3-phenylene diisocyanate; methylene-bis-(4-phenyl isocya-

3

nate); and 1,5-naphthylene diisocyanate. Although not critical to the operability of this reaction, it is often helpful in preparing uniform blown elastomeric sponges to thin the glycol-isocyanate reaction mixture with a small amount of a selected solvent such as acetone or dioxane to permit uniform distribution of the intermediate in the water added subsequently. This solvent must be miscible with the intermediate and with the water and should not be reactive toward the isocyanate groups in the intermediate.

The following examples are given to illustrate the invention. The parts used are by weight.

Example 1

To 120 parts of polyethylene ether glycol of approximately molecular weight 4000 at approximately 70° C., are added slowly with agitation 40 parts of 2,4-toluylene diisocyanate. The reaction mass is stirred at 70° C. for 4 hours. A red-brown, sticky, viscous liquid is obtained. When cooled to room temperature this intermediate is a pale yellow-brown wax.

When 50 parts of this intermediate are dissolved in 150 parts of water at about 35° C., within 1 minute foaming and frothing of the solution occurs, leading rapidly to the formation of a spongy mass.

Example 2

Example 1 is repeated, with the reaction to form the intermediate carried out under a dry nitrogen blanket to maintain anhydrous conditions. This intermediate is stored in a desiccator prior to reaction with water to give a pale, yellow-brown sponge as described in Example 1.

Repeating this example and using m-phenylene diisocyanate or methylene-bis-(4-phenyl isocyanate) instead of 2,4-toluylene diisocyanate, produces blown elastomeric sponges having similar properties.

Likewise, similar sponges are produced by substituting polyethylene ether glycol of molecular weight 6000 or polypropylene ether glycol of molecular weight 750 or 1200 for the polyethylene ether glycol of molecular weight 4000.

Example 3

To 50 parts of the intermediate of Example 2, is added sufficient acetone to form a viscous solution. To this solution is added 150 parts of water at 25° C. Frothing of the milky suspension occurs almost immediately and a cream-colored, resilient, tough sponge is obtained. This sponge is more uniform than that of Examples 1 and 2.

Example 4

Following the procedure of Example 2, 300 parts of the same polyethylene ether glycol reacts with 150 parts of the same diisocyanate for 2 hours at 70° C. After cooling to room temperature in a desiccator this material changes to a very viscous, semi-solid.

To 25 parts of the intermediate of this example is added enough acetone to form a viscous solution when warmed on a steam bath. This solution is removed from the bath and 75 parts of water at 25° C. is added, and the milky suspension is stirred vigorously. Foaming occurs promptly to produce a resilient, white-creamed colored elastomeric sponge which is more uniform in texture than the products of Examples 1 and 2, but less resilient and rubbery than the sponge of Example 3.

Example 5

To 30 parts of the intermediate of Example 2 is added sufficient acetone to make a viscous solution. To this solution is added 45 parts of water at room temperature. A sponge is promptly formed. This sponge when dried in vacuo at room temperature does not retain its original shape as well as the sponge of Example 3 dried in a similar manner.

4

Example 6

Following the procedure of Example 3, a sponge is prepared in a spherical flask to produce a resilient rubbery sphere.

As illustrated in the above examples, where the cold or cool water maintained at approximately 0° to approximately 40° C. is added to the polymerization mass, the rate of the reaction by which cross links are formed and the carbon dioxide is involved is controlled so that the carbon dioxide in this case is trapped inside of the elastomer, forming the closed cell sponge structure.

It has been found on testing the reaction mass as the water is added that it is slightly acid so that the evolution of the carbon dioxide takes place in a very dilute acidic aqueous solution. In carrying out the process above described and illustrated in the examples, the amount of water used can be varied, for it has been found that from 100 parts of water per 100 parts of reaction mass, to 600 parts of water per 100 parts of reaction mass, results in a product having the sponge-like properties as distinguished from the mass or clump formation produced in copending application Serial No. 237,660, now abandoned.

This invention provides the manufacture of tough, elastomeric sponges which have many uses. They may be cast in molds of any desired shape to give sheets, rods, tubes, spheres or other shaped articles, or articles of the desired shape may be cut from the blocks of sponge already formed.

The elastomeric articles of this invention maintain resilience at very low temperatures, such as -20° C. In fact, at temperatures as low as -70° C. these products still exhibit some degree of resilience and can be flexed or bounced without breaking.

The firmness of these sponges, combined with their toughness, makes them useful for shock absorption in a wide variety of applications, and, because the cells are not communicating, these sponges afford greater insulation than the open cell type.

I claim:

1. An elastomeric sponge material obtained by reacting from 100 to 600 parts by weight of water with 100 parts by weight of the reaction product of a polyalkylene ether glycol having a molecular weight of from 750 to 6000 and a molar excess of an arylene diisocyanate.
2. An elastomeric sponge material obtained by reacting from 100 to 600 parts by weight of water with 100 parts by weight of the reaction product of a polyethylene ether glycol having a molecular weight of about 4000 to 6000 and a molar excess of an arylene diisocyanate of the benzene series.
3. An elastomeric sponge material obtained by reacting from 100 to 600 parts by weight of water with 100 parts by weight of the reaction product of a polypropylene ether glycol having a molecular weight of from 750 to 1200 and a molar excess of an arylene diisocyanate of the benzene series.
4. An elastomeric sponge material obtained by reacting approximately 300 parts by weight of water with 100 parts by weight of the reaction product of a polyethylene ether glycol having a molecular weight of about 4000 and 2,4-toluylene diisocyanate.

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PLAINTIFF'S EXHIBIT 10

"Princeton Introduces Novel Polyurethanes Made
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pages 79, 165-166

Pages 742a to 744a

Chemical Engineering

WITH CHEMICAL & METALLURGICAL ENGINEERING

APRIL 1950

VOL. 57 NO. 4

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HOW TO USE READER SERVICE—PAGE 5

entator

CAL ENGINEERING IN INDUSTRY

Joseph A. O'Connor, News Editor

Among fibers with wool-like characteristics that recently been introduced are Union Carbide's Vinal, Du Pont's Orlon, and Terylene, made by Imperial Chemical Industries, Ltd.

A Home Is In the Streets

BRITISH LION—Imperial Chemical Industries, with 12 operating divisions and close to 100,000 workers in the United Kingdom, is the lion of Britain's chemical industry. And now it wants to get into the U.S., to manufacture its dyestuffs and other synthetic chemicals here and also to acquire a ready-made marketing organization for its British-made products.

HUNGRY FOR DOLLARS—Ever since the British pound sterling was devalued last September the giant ICI has been hungry for dollars. Devaluation made ICI prices more competitive and dollars all the more important to stockholders.

HURDLES U. S. BARRIER—So ICI has set itself for a leap it has wanted to take for a long time. Just before the British election, ICI offered to a controlling interest in Arnold, Hoffman & Co., of Providence, R. I. This 135-year old firm, with plants at Charlotte, N. C., Cincinnati, Ohio, and Boston, Mass., turns out dyestuffs, plasticizers, printing gums, sulphonated oils, synthetic resins and wetting agents. Equally significant for ICI, it's an active distributor of chemicals. It is thus that ICI hopes to the U. S. tariff barrier.

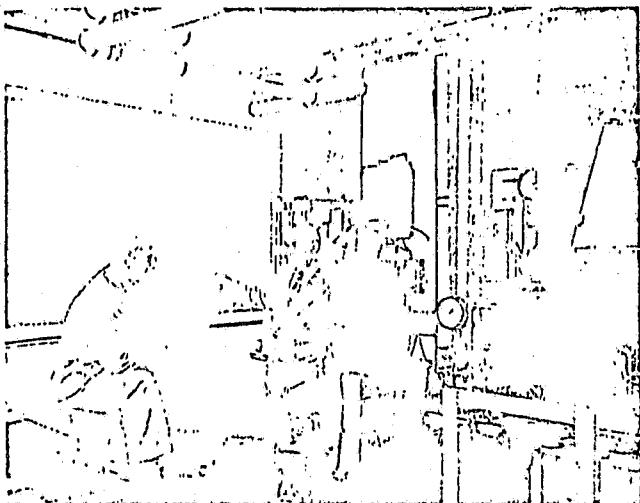
ICI proposes to pay \$55 a share for a minimum two-thirds or a maximum of 70 percent of the outstanding 93,000 shares of Arnold, Hoffman common stock offered in New York at \$20 a share, the par value of \$10.

To finance the deal, ICI will borrow up to \$1 million from Manhattan's Guaranty Trust Co. The loan will be repaid out of Arnold, Hoffman earnings. Hence there is no drain on Britain's scarce dollars.

Besides handling dyestuffs and other products, ICI, Hoffman is to employ ICI manufacturing processes, getting patents and know-how in return for fees.

ELUDING HUNTERS—Of some in the U. S., ICI lion, wise in the ways of the anti-trust jungle,

(Continued)



Skull practice in Princeton's Plastics Laboratories finds Boyd H. Carr, Jr., heading Natcho Vasileff as he runs through reaction that produces new resins they developed.

Princeton Introduces Novel Polyurethanes Made From Castor Oil and Diisocyanate

(165a) From the Plastics Laboratories at Princeton University has come a new series of polyurethane plastics with many promising applications, chief of which so far is as potting compounds for transformers. Not only the Armed Forces, which sponsored the research, but also certain manufacturers of electrical equipment are interested in the potting compounds.

Varying from extremely hard to soft rubbery materials, these plastics exhibit good elastomeric, electrical and physical properties. They are good shock dampeners. Made by reacting castor oil with diisocyanates, these easily prepared plastics appear to be, in general, cross-linked products. They can be handled by casting methods.

Birthplace of these polyurethanes is the Plastics Laboratories at Princeton, a hotbed of research ideas, where graduate students, not a few of them mature and serious veterans who are zeroing in on carefully chosen targets for their life work, are taking advantage of a unique course in plastics engineering. Director of the laboratories is Louis F. Rahm, a genial, communicative man who likes to emphasize the free access to information found in the academic atmosphere. Obviously, he's proud of this latest

achievement of two of his associates, research group leader Natcho Vasileff and one of his bright young men.

FLOOD OF ORGANIC

No sooner does Vasileff get you seated across from him at his desk in a little office at the rear of the laboratory than he reaches for a pencil, starts drawing structural formulas rapidly on the back of an envelope.

"Diisocyanates react with compounds containing poly-reactive hydrogens, compounds like diamines or glycols," he explains. "The double bond between the nitrogen and the carbon in the isocyanate group is the reactive point. There's an isocyanate group at each end of the diisocyanate, of course." He speaks with an accent. Natcho Vasileff left his native Bulgaria in 1923 to come to the United States. During World War II, he worked in the U. S. Signal Corps laboratories at Fort Monmouth, N. J.

"Take the reaction of a diisocyanate with an alcohol," he says. More structural formulas cover the back of the envelope. When he looks up, his brown eyes shine excitedly. "The active hydrogen from the alcohol hooks onto the nitrogen in the isocyanate group, so. And the rest of the alcohol attaches to the carbon. No

more double bond, just a single one between the nitrogen and the carbon. It can happen at each end of the diisocyanate."

He thumbs through a fat organic book, finds a reference. "The Germans used these reactions. They turned to the polyurethanes when they were looking for materials like nylon."

Had Vasileff himself hit upon these polyurethane plastics as the potting compounds the Signal Corps needed to ease its transformers? The flood of organic chemistry is dammed. He pauses and beams. "It was Carr. Carr is one of my boys. He should be along soon."

Presently he is, Boyd H. Carr, Jr., who was born in a town that chemical enterprise helped to build, Midland, Mich., is a young research assistant working in Vasileff's group. All told, Director Rahm has five research groups at work in the laboratories.

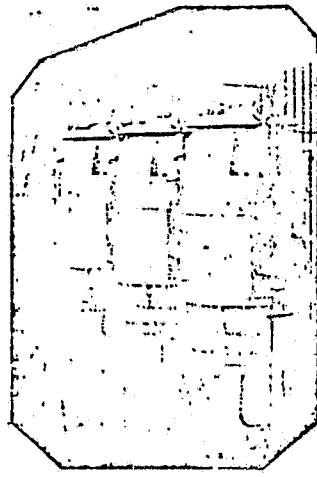
DISCOVERY

It turns out that Carr had been looking for a binder that could be loaded with TiO_2 to yield a non-brittle, high-K, low-loss product. Polyurethanes seemed likely materials. To make one that would be more resilient and rubber-like, he had reacted castor oil with a diisocyanate. The resulting product, being resilient, tough, more or less thermoset and somewhat elastomeric, as well as easy to prepare and approximately neutral in pH, looked mighty interesting to Carr. For despite his bow-tied-and-jacketed campus casualness, Boyd Carr, with his sharp brown eyes, was quick to realize that this might be the potting compound Princeton was hunting for the Signal Corps. He did not discard the stuff. Instead, the investigation, guided by Vasileff and Rahm, took a new tack.

NOW THEY'RE MADE

Vasileff resumes his explanation. "What we do is react castor oil with a diisocyanate. Castor oil is basically a trihydroxy alcohol, and it forms cross linkages with diisocyanates. The cross linkages make the plastic material thermosetting. Actually, castor oil consists of about 80 percent of the triricinoleic ester of glycerine. But for our purposes we assume it to be 100 percent triricinolein glyceride with a molecular weight of 932. The reactive points in it are at the $-OH$ group on the twelfth carbon atom of each ester group. We react this castor oil with TDI. That's tolylene diisocyanate, the meta compound, with a molecular weight of 174. We get it from Monsanto. How much castor oil and TDI

(Continued)



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NEW PRODUCTS, cont. . .

do we use? The proportions are varied. But we use from 75 to 80 percent by weight of castor oil and 25 to 20 percent of TDI.

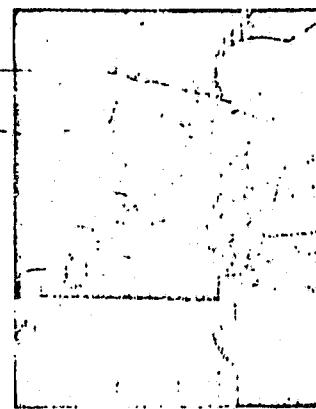
"The reaction is exothermic, but not vigorous. Temperature and pressure? The polymerization will go at room temperature. It takes place at atmospheric pressure. But under reduced pressure it's easier to get rid of any CO₂. The CO₂ comes from the reaction of impurities like water or free acid in the castor oil with the diisocyanate. As a catalyst, we've used about 1 percent by weight of Minnesota Mining's Sylon RD 602. That's di-tertiary butoxy diamino silane. It's a diamine, so it reacts with TDI. And it speeds up the cure."

In the wake of the initial research after Carr's discovery came many other experiments designed to explore possible structural modifications. Resins were made from castor oil, TDI and other glycols. In addition, castor oil itself was varied through partial esterification and used in forming some polyurethane resins. Improved physical and electrical properties were achieved by modifying castor oil-TDI resins with hexamethylene glycol, glycerine and especially 2-ethyl hexanediol-1,3.

PROPERTIES

Best low-loss properties are possessed by the castor oil-TDI resin modified with hexamethylene glycol. It is hard, brittle and fairly thermoplastic. The resin with the lowest loss qualities in combination with good physical properties is one made from castor oil, TDI and 2-ethyl hexanediol-1,3. It has good electrical and mechanical properties. It has good chemical resistance, notwithstanding caustic and mineral acids, together with fair solvent resistance, good heat resistance and a neutral pH action. Its shrinkage on gelling is negligible, and it has fairly good qualities at low temperatures.

Best potting compound of those tested was the castor oil-TDI resin modified with 2-ethyl hexanediol-1,3. Five transformers encased in it came through the tests required by Army-Navy Specification JAN-T-27 successfully. The potted transformers passed the 5-cycle test with little effect on electrical properties. No internal shearing was found, and the beakers containing the resin-enclosed transformers were not broken by thermal action. After the 5 cycles, the potted transformers were immersed in saturated salt water at room temperature for 66 hr, with little effect on insulation resistance.



Transformer potted in resin.

After seven weeks in an oven at 140 deg. C. one of these diisocyanate-castor oil resins modified with a little octylene glycol showed no change in electrical properties. It hardened somewhat, however, and darkened slightly. Normally, these resins are clear and yellowish. They look and feel rubbery, but they do not bounce. Despite their high compressive strength, these plastics absorb shock. They have been used to protect thermometers. Thin sheets will dampen vibrations and noises. When they are cast, they take the shape wanted and set up quickly, with little shrinkage. They stick to materials like cloth and leather.

The foregoing materials were produced in the course of contract research at Princeton sponsored by the Army, Navy and Air Force.—Plastics Laboratories, Princeton University, 30 Charleton St., Princeton, N.J.

MILL-TESTED:

Neoprene Additive

(166a) A new type of Du Pont neoprene, especially developed for treating paper, increases the strength and chemical resistance of the finished paper. The process for adding it to the pulp has been mill-tested.

Both the neoprene and process for its addition were developed in the Deepwater Point, N.J., laboratories of Du Pont. Five of the company's rubber researchers, R.H. Walsh, H.I.I. Abernathy, W.W. Pockman, J.R. Calloway and E.P. Hartsfield, reported details about both developments at the recent New York meeting of the Technical Association of the Pulp & Paper Industry.

A practical process has been developed for adding neoprene to paper at the beater. It has undergone various

(Continued)

FROM

**A very
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**THE DIVI
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**Hydraulic
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**Other op
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oils, gre**

**333
Eastern Div
Los Angeles**

PLAINTIFF'S EXHIBIT 11

British Patent No. 793,780

Pages 745a to 755a

Elizabeth the Second by the Grace of God of the United Kingdom of Great Britain and Northern Ireland and of Her other Realms and Territories Queen, Head of the Commonwealth, Defender of the Faith: To all to whom these presents shall come greeting:

WHEREAS Monsanto Chemical Company, a corporation organised under the laws of the State of Delaware, United States of America, of 1700 South Second Street, City of St. Louis, State of Missouri, United States of America

(hereinafter referred to as the said applicants) have prayed that a patent may be granted unto them for the sole use and advantage of an invention for Production of condensation polymers

AND WHEREAS the said applicants (hereinafter together with their successors, and assigns, or any of them referred to as the patentees) have declared that there is no lawful ground of objection to the grant of a patent unto them:

AND WHEREAS the complete specification has particularly described the invention:

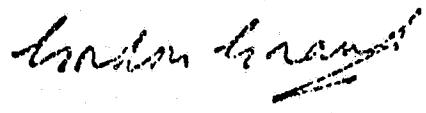
AND WHEREAS We, being willing to encourage all inventions which may be for the public good, are graciously pleased to condescend to their request:

NOW YE, THEREFORE, that We, of our especial grace, certain knowledge, and mere motion do by these presents, Us, our heirs and successors, give and grant unto the said patentees our especial licence, full power, sole privilege, and authority, that the said patentees by themselves, their agents, or licensees, and no others, may subject to the conditions and provisions prescribed by any statute or order for the time being in force at all times hereafter during the term of years herein mentioned, make, use, exercise and vend the said invention within our United Kingdom of Great Britain and Northern Ireland, and the Isle of Man, and that the said patentees shall have and enjoy the whole profit and advantage from time to time accruing by reason of the said invention during the term of sixteen years from the date hereunder written of these presents: AND to the end that the said patentees may have and enjoy the sole use and exercise and the full benefit of the said invention, We do by these presents for Us, our heirs and successors, strictly command all our subjects whatsoever within our United Kingdom of Great Britain and Northern Ireland, and the Isle of Man, that they do not at any time during the continuance of the said term either directly or indirectly make use of or put in practice the said invention, nor in anywise practise the same, without the consent, licence or agreement of the said patentees in writing under their hands and seals, on pain of incurring such penalties as may be justly inflicted on such offenders for their contempt of this our Royal command, and of being answerable to the patentees according to law for their damages thereby occasioned:

PROVIDED ALWAYS that these letters patent shall be revocable on any of the grounds from time to time by law prescribed as grounds for revoking letters patent granted by Us, and the same may be revoked and made void accordingly:

PROVIDED ALSO that nothing herein contained shall prevent the granting of licences in such manner and for such considerations as they may by law be granted: AND lastly, We do by these presents for Us, our heirs and successors, grant unto the said patentees that these our letters patent shall be construed in the most beneficial sense for the advantage of the said patentees.

IN WITNESS whereof We have caused these our letters to be made patent
as of the sixt^h day of August
one thousand nine hundred and fifty-four and to be sealed.



Comptroller-General of Patents,
Designs, and Trade Marks.

AMENDED SPECIFICATION

As amended in accordance with the Decision of the Superintending Examiner
for the Comptroller General dated the twenty-eighth day of October 1963, under
Section 14 of the Patents Act, 1949.

PATENT SPECIFICATION

NO DRAWINGS

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R33C(4:9:10:11:12:13), R33P.

International Classification:—C08g.

COMPLETE SPECIFICATION

Production of Condensation Polymers

We, MONSANTO CHEMICAL COMPANY, a corporation organised under the Laws of the State of Delaware, United States of America, of 1700 South Second Street, City of St. Louis, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of condensation polymers from substances containing a plurality of isocyanate or isothiocyanate groups.

According to the present invention there is provided a process for the production of a substantially bubble-free plasticised urethane or thiourethane condensation polymer which comprises reacting an excess of an organic polyisocyanate or polyisothiocyanate with an organic polyhydroxy or polymercapto compound in the presence of a non-reactive organic compound so as to form a solid or viscous liquid solution in the non-reactive organic compound of a relatively stable initial condensation product containing at least one urethane or thiourethane group and also at least one free isocyanate or isothiocyanate group and thereafter heating the said solution in the substantial absence of moisture or other added reactive material to form said condensation polymer, said non-reactive compound having a boiling point of at least 200°C. at atmospheric pressure and being soluble in the initial condensation product and the condensation polymer.

By substantial absence of moisture is meant insufficient water to be of any practical significance as regards the formation of foam or

bubbles in the final plasticised urethane or thiourethane condensation polymer.

The invention also provides a process for the production of a plasticised urethane or thiourethane condensation polymer foam which comprises reacting an excess of an organic polyisocyanate or polyisothiocyanate with an organic polyhydroxy or polymercapto compound in the presence of a non-reactive organic compound so as to form a solid or viscous liquid solution in the non-reactive organic compound of a relatively stable substantially bubble-free initial condensation product containing at least one urethane or thiourethane group and also at least one free isocyanate or isothiocyanate group and thereafter treating the said solution with a compound capable of yielding in aqueous solution ionisable hydroxyl or substituted hydroxyl groups or a precursor thereof to form said condensation polymer foam, said non-reactive organic compound having a boiling point of at least 200°C. at atmospheric pressure and being soluble in the initial condensation product and the condensation polymer.

As illustrative examples of suitable polyhydroxy compounds for use in the production of condensation polymers containing urethane groups, there may be mentioned glycols such as ethylene glycol, propylene glycol, butylene glycol-2,3, butylene glycol-1,3, 2-methyl pentanediol-2,4, 2-ethylhexanediol-1,3, hexamethylene glycol, styrene glycol, N-phenyldiethanolamine, catechol, resorcinol, 2,2-bis(4-hydroxyphenol)propane, p,p'-dihydroxy diphenyl, decamethylene glycol; polyglycols (ether glycols) such as polyethylene glycols, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycols having

[Price 4s. 6d.]

- average molecular weights of 200, 400 and 600; polypropylene glycols, dipropylene glycol, tripropylene glycol, polypropylene glycols having average molecular weights of 400, 750, 1200 and 2000; carbowaxes 1000, 1000 W, 1500; monoethers of trihydroxy compounds such as glycercyl- α -allyl ether, glycercyl- α -phenyl ether, glycercyl- α -isopropyl ether; hydroxy esters such as an ester prepared from 1 mol of dibasic acid and 2 mols of a glycol or polyglycol, a polyester prepared so that the molar ratio of glycol or polyglycol to the dibasic acid is between 2 and 1, an ester prepared from 1 mol of a dimer acid and 2 mols of a glycol or polyglycol, an ester prepared from a hydroxy acid and a glycol or polyglycol so that the molar ratio of the glycol or polyglycol to the hydroxy acid is between 0.5 and 1 and an ester prepared from 1 mol of a trihydroxy compound and 1 mol of a monobasic acid, such as the monoglyceride of oleostearic acid; trihydroxy compounds such as glycerine, triethanolamine, pyrogallol and phloroglucinol; alkylene oxide condensates of glycerine, triethanolamine, pyrogallol and phloroglucinol; monoethers of tetrahydroxy compounds; esters prepared from hydroxy acid and a trihydroxy compound so that the molar ratio of the latter to the former is between 0.33 and 1, such as glycerine triricinoleate, esters prepared from 1 mol of a monobasic acid and 1 mol of a tertihydroxy compound; tetrahydroxy compounds such as pentaerythritol, alkylene oxide condensates of pentaerythritol, esters prepared from 1 mol of a dibasic acid and 2 mols of a trihydroxy compound; pentahydroxy compounds, such as arabitol and xylitol; hexahydroxy compounds such as sorbitol, dulcitol and mannitol.
- Examples of polymercapto compounds which may be reacted with polyisocyanates to form thiourethane condensation polymers are dimercaptoethane, 1,2,3 - trimercaptopropane, 1,2,3 - trimercaptobutane, 1,5 - dimercapto-3 - mercaptomethylpentane, 1,6 - dimercaptohexane, 1,10 - dimercaptohexane, 1,6 - dimercapto - 3 - methylhexane, 1,4 - dimercaptobenzene, dimercaptoxylylene, dimercaptoresorcinol and polyvinyl mercaptan.
- Examples of polyisocyanates and polyisothiocyanates which may be employed in the production of condensation polymers containing urethane or thiourethane groups are polymethylene di-isocyanates and di-isothiocyanates, such as ethylene di-isocyanate, trimethylene di-isocyanate, tetramethylene di-isocyanate and pentamethylene di-isocyanate; and the corresponding di-isothiocyanates; alkylene di-isocyanates and di-isothiocyanates, such as propylene-1,2-di-isocyanate, butylene-1,2-di-isocyanate, butylene-1,3-di-isocyanate, butylene-2,3-di-isocyanate and butylene-1,3-di-isothiocyanate; alkylidene di-isocyanates and di-isothiocyanates, such as ethylidene di-isocyanate butylene di-isocyanate and

ethylidene di-isothiocyanate; cycloalkylene di-isocyanates and di-isothiocyanates, such as cyclopentylene - 1,3 - di-isocyanate, cyclohexylene - 1,2 - di-isocyanate, cyclohexylene - 1,4 - di-isocyanate, and cyclohexylene - 1,2 - di-isothiocyanate; cycloalkylidene di-isocyanates and di-isothiocyanates, such as cyclopentylidene di-isocyanate, cyclohexylidene di-isocyanate and cyclohexylidene diisothiocyanate; aromatic di-isocyanates and di-isothiocyanates, such as meta-phenylene di-isocyanate, para-phenylene di-isocyanate, naphthylene-1,4-di-isocyanate, diphenylene-4,4'-di-isocyanate and para-phenylene di-isothiocyanate; aliphatic-aromatic di-isocyanates or di-isothiocyanates, such as xylylene-1,4-di-isocyanate, xylylene-1,3-di-isocyanate, 4,4'-diphenylenemethane di-isocyanate, 4,4'-diphenylenepropane di-isocyanate and xylylene-1,4-di-isothiocyanate.

The urethane condensation polymers containing urethane and/or thiourethane groups are prepared by reacting an organic compound of the general formula: R(NCX)_n with an organic polyhydroxy and/or polymercapto compound in the proportions providing a ratio of —NCX groups to active hydrogen atoms which is greater than 1:1 and is desirably at least 1.1:1. The ratio may be n:1 where n is the number of isocyanate or isothiocyanate groups in the molecule of the polyisocyanate or polyisothiocyanate. Preferably these reactants are employed in the proportions providing a ratio of —NCX groups to active hydrogen atoms of from 1.5:1 to n:1 and more preferably at least 2:1. The initial products obtained by this reaction are condensation products which contain urethane and/or thiourethane groups and also free isocyanate and/or isothiocyanate groups.

The condensation polymers are relatively brittle resins and, in accordance with this invention they are plasticised and rendered more flexible by effecting their preparation in the presence of a non-reactive organic material which is soluble in the condensation product produced and which boils at a temperature not lower than 200°C., and preferably not lower than 250°C., at atmospheric pressure. This yields a solid or a viscous liquid solution of the condensation product which is stable for a considerable period of time if stored at room temperature in tightly closed containers. However, when heated in the manner herein described, the solution is converted into a complex resinous polymer plasticised by the above-mentioned plasticiser.

As illustrative examples of non-reactive organic liquids and solids which are soluble in the condensation products and may be used in the practice of this invention, there may be mentioned trichlorobenzene, chlorinated diphenyl, chlorinated 1,3,3-trimethyl-1-

phenylindane, chlorinated 1,3,3,6-tetramethyl-1(4'-methylphenyl)indane, dimethoxy tetraethylene glycol, diethyl phthalate, dibutyl phthalate, diamyl phthalate, butyl benzoyl benzoate, butyl phthalyl butyl glycolate, N-ethyl-para-toluene sulphonamide, diphenyl ortho-diphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, dibutyl sebacate, dibenzyl sebacate, partially hydrogenated liquid aromatic hydrocarbon mixtures such as those disclosed in U.S. Patent Specification No. 2,364,719, expoxidized safflower oil and petroleum and coal tar oils which boil above 200°C., and preferably above 250°C., at atmospheric pressure. In fact, any organic liquid or solid boiling above 200°C. which is soluble in the above described condensation products containing urethane groups and the final condensation polymer may be employed in the practice of the present invention.

The plasticised condensation polymers produced in accordance with the present invention cannot be produced by first forming the polymerised or cured organic compound containing a urethane or thiourethane group and then incorporating the cured product with the plasticiser.

The curing of the solid or viscous liquid solution of the above-mentioned condensation product admixed with plasticiser is effected by heating, in the substantial absence of moisture or other added reactive materials containing reactive hydrogen atoms, and with or without a catalyst. This heating is sufficient to effect a reaction between at least one urethane or thiourethane group and an isocyanate and/or an isothiocyanate group of the same or another molecule containing both types of functional groups.

The curing operation is carried out in the absence or presence of a catalyst and at temperatures varying from room temperature up to about 225°C., preferably from 60°C. to 200°C. and most preferably from 100°C. to 125°C.

The plasticised polymers obtained vary from soft resinous gels to hard brittle resins, depending upon the amount and type of components used in their production.

In the production of plasticised products in accordance with this invention, the liquid or solid plasticiser is desirably employed in an amount varying from 20% to 80% by weight, basis total weight, and within these limits 40% to 60% by weight is preferred. If desired, larger or smaller amounts may be employed in order to effect the desired degree of plasticisation.

The polymers produced in accordance with the present invention may be in the form of bubble-free resinous compositions or highly cellular resinous foams, the character of the products being dependent upon the conditions of manufacture.

For example, if a substantially bubble-free resin is desired, heating the condensation product containing at least one urethane and/or thiourethane group and an isocyanate and/or an isothiocyanate group and the non-reactive organic materials soluble therein is carried out in the absence of a catalyst. On the other hand, if a cellular product is desired, the curing of the unfoamed initial condensation product is effected in the presence of a catalyst which in aqueous solution yields ionisable hydroxyl or substituted hydroxyl groups or a precursor of such a compound. These catalysts are disclosed and their use claimed in our co-pending application No. 773,897: the catalysts which may be used comprise an oxide, hydroxide or alcoholate of an alkali metal or a quaternary ammonium base.

The following examples illustrate the invention and the manner in which it may be performed:

Manufacture of Substantially Bubble-Free Gels and Resins

EXAMPLE I

11.1 parts of triethanolamine (1 mol) was reacted with 38.9 parts of meta-tolylene diisocyanate (3 mols) in the presence of 50 parts of chlorinated diphenyl containing 42% chlorine. The resulting mixture consisted of a white solid suspended in a yellow liquid. This liquid was separated and heated in an oven at a temperature of 100°C. for 12 hours and a hard, clear resin was obtained.

A sample of this resin was held in a Bunsen flame and it burned with a smokey flame without melting but was extinguished as soon as it was removed.

EXAMPLE II

55.5 parts of triethanolamine (1 mol) and 250 parts of chlorinated diphenyl containing 42% chlorine were mixed thoroughly in a flask and then 194.5 parts of metatolylen diisocyanate (3 mols) was added with stirring. During this addition, the reaction temperature was maintained at a value not exceeding 50°C. This resulted in the production of a slurry of a solid material which was separated from the liquid by filtering. A sample of the liquid reaction product was placed in an oven at 100°C. and, after 18 hours the liquid solidified. The solubility of this solid product in various liquids was determined and it was found that the resin did not dissolve in boiling solvents such as water, methanol, acetone, hexane, benzene, carbon tetrachloride and ethyl acetate.

EXAMPLE III

A slurry containing 39.1 parts of diethanolamine (1 mol) and 250 parts of chlorinated diphenyl containing 42% chlorine was reacted with 194.5 parts of meta-tolylene diisocyanate to form a liquid product containing a relatively small proportion of solid material which

was separated by filtering. The liquid product was then heated in an oven at 100°C. until it solidified into a hard, clear resin.

EXAMPLE IV

5 38.9 parts of meta-tolylene diisocyanate (3 mols) and 11.1 parts of triethanolamine (1 mol) were reacted together in the presence of 50 parts of nuclear chlorinated isopropyl-diphenyl containing 42% of chlorine. The 10 reaction product consisted of a liquid containing a relatively small proportion of solids which were removed by filtration. The liquid portion of the reaction product was heated in an oven at 100°C. for a period of 24 hours and a soft, yellow resinous gel was obtained.

EXAMPLE V

11.1 Parts of triethanolamine (1 mol) and 38.9 parts of meta-tolylene diisocyanate (3 mols) were reacted together in the presence of 20 50 parts of the following:

- Sample No. 1 Chlorinated diphenyl containing 21% chlorine
- Sample No. 2 Chlorinated diphenyl containing 32% chlorine
- 25 Sample No. 3 Chlorinated diphenyl containing 42% chlorine
- Sample No. 4 Chlorinated diphenyl containing 48% chlorine
- 30 Sample No. 5 Chlorinated diphenyl containing 54% chlorine
- Sample No. 6 Chlorinated diphenyl containing 60% chlorine
- 35 Sample No. 7 Chlorinated naphthalene

On heating to a temperature of 100°C. for 35 a period of 20 hours, Sample Nos. 1-5 and 7 formed clear, amber resins whereas Sample No. 6 produced a sticky, opaque resin.

EXAMPLE VI

40 55.5 Parts of triethanolamine (1 mol) and 19.5 parts of meta-tolylene diisocyanate (3 mols) were reacted together in the presence of 250 parts of chlorinated diphenyl containing 42% chlorine. This reaction was carried out at room temperature using chlorinated diphenyl which had been previously saturated with hydrogen chloride gas. This resulted in the production of a liquid containing a relatively small proportion of solids which were removed by filtration. A sample of this liquid product was heated at a temperature of 100°C. for 3.25 hours to form a thick gel and for a total of 4.25 hours to form a very hard and brittle resin which was substantially free from bubbles.

EXAMPLE VII

45 8.3 Parts of triethanolamine (1 mol) and 41.7 parts of p,p'-diisocyanatodiphenylmethane (3 mols) were reacted together in the presence of 50 parts of chlorinated diphenyl containing 42% chlorine. The

resulting reaction product was placed in a 100°C. oven and heated for about 5 hours. This resulted in the production of a hard, clear, yellow resin similar to that obtained with meta-tolylene diisocyanate.

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EXAMPLE VIII

11.1 Parts of triethanolamine (1 mol) was dissolved in 50 parts of molten diphenyl and to the resulting solution 38.9 parts of meta-tolylene diisocyanate (3 mols) was added. The 70 product obtained as a result of the ensuing reaction was heated for 24 hours at 100°C. and a hard, clear, light yellow resin was obtained.

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EXAMPLE IX

10.3 Parts of castor oil was reacted with 4.1 parts of meta-tolylene diisocyanate in the presence of chlorinated diphenyl containing 42% chlorine, the reaction taking place at room temperature. The product of this 80 reaction was a clear, viscous liquid which, on heating for 40 hours at 125°C., yielded a flexible, bubble-free resin.

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EXAMPLE X

Meta-tolylene diisocyanate and the condensate of 6.6 mols of propylene oxide with 1 mol of glycerine were reacted together in a molar ratio of 3 mols of the diisocyanate to 1 mol of the condensate, the reaction taking place in the presence of a sufficient amount of chlorinated diphenyl containing 42% chlorine to yield a 50% solution of adduct. On heating for 2.25 hours at 140°C., a sample of this solution yielded a tough, rubbery and resinous gel.

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EXAMPLE XI

Meta-tolylene diisocyanate containing 0.23% of hydrolysable chlorine was reacted with the following alkylene oxide condensates of glycerine in a molar ratio of 3 mols of the isocyanate to 1 mol of the condensate, the reaction taking place in the presence of sufficient amount of chlorinated diphenyl containing 42% chlorine to yield a 50% solution of the adduct.

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Condensate of 3.1 mols of propylene oxide with 1 mol of glycerine	105
Condensate of 13.2 mols of propylene oxide with 1 mol of glycerine	
Condensate of 12 mols of ethylene oxide with 1 mol of glycerine	110
Condensate of 3 mols of ethylene oxide with 1 mol of glycerine	

The products of these reactions were all clear, viscous liquids except the solution of adduct prepared from 3.1 mols of propylene oxide with 1 mol of glycerine, which was a cloudy, viscous liquid. On being heated to 150°C. for 3 hours, 4.75 hours, 7.5 hours and 4.75 hours, respectively, these reaction products formed gels which, on continued heating for a total of 23 hours at the same

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temperature, produced flexible, bubble-free resins that decreased in flexibility with decreasing molecular weight of the condensate used in the preparation of the adduct.

EXAMPLE XII

Solutions of the following compositions, when heated for 23 hours at 125°C., yielded substantially bubble-free products which varied with decreasing amounts of solvent from a soft jelly to a tough, flexible resin.

Adduct	% By Weight of Adduct	% By Weight of Chlorinated Diphenyl Containing 42% Chlorine
Adduct of 3 mols of meta-tolylene diisocyanate with 1 mol of the condensate of 13.2 mols of propylene oxide with 1 mol of glycerine	20	80
"	35	65
"	65	35
"	80	20

EXAMPLE XIII

Solutions of the following compositions, when heated for 23 hours at 125°C., produced

substantially bubble-free, brittle resins which increased in hardness as the amount of solvent was decreased.

Adduct	% By Weight of Adduct	% By Weight of Chlorinated Diphenyl Containing 42% Chlorine
Adduct of 3 mols of meta-tolylene diisocyanate with 1 mol of the condensate of 3.1 mols of propylene oxide with 1 mol of glycerine	20	80
"	35	65
"	65	35
"	80	20

EXAMPLE XIV

- 20 Substantially 3 mols of meta-tolylene diisocyanate was reacted with the condensation product of 13.2 mols of propylene oxide with 1 mol of glycerine in the presence of a sufficient amount of the following chlorinated compounds numbered 1—6, inclusive, to yield
- 25 a 50% solution of the resulting adducts. In the remaining cases, namely, 7—9, inclusive, the condensation product was mixed with similar amounts of the melted chlorinated compound and then reacted with the meta-tolylene diisocyanate.

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Physical Appearance of Adduct

1.	Unrefined chlorinated diphenyl containing 48% by weight of chlorine	Dark liquid
2.	Chlorinated diphenyl containing 21% chlorine	Clear, viscous liquid
3.	Chlorinated diphenyl containing 32% chlorine	" "
4.	Refined chlorinated diphenyl containing 48% chlorine	" "
5.	Refined chlorinated diphenyl containing 54% chlorine	" "
6.	Refined chlorinated diphenyl containing 60% chlorine	Very viscous, clear liquid
7.	Chlorinated mixture of 60% diphenyl and 40% distilled high boiler containing 65% chlorine	Clear, extremely viscous liquid
8.	Chlorinated isomeric terphenyl mixture containing 42% chlorine	Clear, extremely viscous liquid
9.	Chlorinated distilled high boiler containing 60% chlorine	Clear solid

The products obtained as a result of these reactions were heated at a temperature of 125°C. until a gel was formed, whereupon the heating was continued for a total of 13 hours to convert the gel into a resin. The time required to gel the above products and the type of resins formed are indicated in the following table.

Sample No.	Total Time Required For Sample to Gel	Type of Resin Formed
1	Greater than 6 hours	Dark, flexible, soft, bubble-free resin
2	2.5 hours	Flexible, bubble-free resin
3	1.5 hours	Flexible, bubble-free resin
4	1.5 hours	Flexible, bubble-free resin
5	Greater than 6 hours	Soft, flexible, bubble-free resin
6	Greater than 6 hours	Soft, flexible, resin with a few bubbles
7	1.5 hours	Hard, flexible, bubble-free resin
8	2.5 hours	Flexible, bubble-free resin
9	2.5 hours	Brittle resin with a few bubbles

EXAMPLE XV

Substantially 3 mols of meta-tolylene diisocyanate was reacted with 1 mol of the condensation product of 13.2 mols of propylene oxide with 1 mol of glycerine, the reaction taking place in the presence of a sufficient amount of the following organic liquids to form a 50% solution of the adduct having the properties indicated:

Sample No.	Physical Properties of Solution of Adduct
1.	Partially hydrogenated aromatic liquid mixture having a specific gravity of 1.004 at 250°C., a refractive index of 1.5600 at 25°C. and a boiling range of 340°C. to 390°C. at atmospheric pressure
2.	Chlorinated 1:3:3-trimethyl-1-phenylindane
3.	Epoxidised safflower oil
4.	Tricresyl phosphate
5.	2-ethylhexyl diphenyl phosphate
6.	Butyl phthalyl butyl glycolate
7.	Dimethoxy tetraethylene glycol
	Clear, viscous liquid
	" " "
	" " "
	" " "
	" " "
	" " "
	Clear liquid

The above products were heated at a temperature of 125°C. until they were gelled and then the gels were heated up to a total of 22.5 hours to convert them into resins. The time required for the products to gel and the properties of the resins are given in the following table.

	Time Required for Sample to Gel, Hrs.	Type of Resin Formed
1	Greater than 6.5	Flexible resin with some tendency for organic liquid to exude
2	3.5	Flexible resin
3	1	" "
4	5.5	" "
5	3	" "
6	5.5	" "
7	More than 2.5	" "

EXAMPLE XVI

3 Mols of meta-tolylene diisocyanate was reacted with 1 mol of the condensate of 13.2 mols of propylene oxide with 1 mol of glycerine, the reaction being carried out in the presence of a sufficient amount of tricresyl phosphate or chlorinated diphenyl containing 42% chlorine to yield 20%, 50%, and 80% solutions of the adduct. A similar reaction was carried out using 3 mols of meta-tolylene diisocyanate and 1 mol of the condensate of 3.1 mols of propylene oxide with 1 mol of glycerine. The resulting reaction products were further heated to yield resinous polymers plasticized by the solvent employed.

Similar products were also made by adding the above condensates to the following molten

chlorinated compounds, reacting meta-tolylene diisocyanate with the condensate in the molar ratio indicated above and then heating the resulting products to convert them into plasticised resinous polymers.

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1. A chlorinated mixture consisting of 60% diphenyl and 40% distilled high boiler containing about 65% chlorine
2. A chlorinated isomeric terphenyl mixture containing 42% chlorine
3. Chlorinated distilled high boiler containing 60% chlorine

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In order to determine the temperature characteristics of these resins, they were cooled to -12°C. and heated to 200°C. and 300°C.

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on a Fisher-Johns melting point apparatus. All of these resins were liquid or extremely soft at 300°C. and gave off vapour. At 200°C. very little change in the nature of the resins was noted, but at -12°C., all of these resins were quite brittle.

EXAMPLE XVII

8 Parts of the condensate of 13.2 mols of propylene oxide with 1 mol of glycerine was reacted with 7 parts of p,p'-diisocyanato-diphenylmethane which had been pretreated with hydrogen chloride gas, the reaction being executed in the presence of 15 parts of chlorinated diphenyl containing 42% chlorine. The product of this reaction was a soft, sticky, gummy, cloudy liquid. This product was heated at 125°C. for a period of 15 hours and a clear, flexible resin substantially free from bubbles was obtained.

EXAMPLE XVIII

A mixture of 15 parts of chlorinated diphenyl containing 42% chlorine and about 15 parts of the adduct of about 3 mols of meta-toluylene diisocyanate with 1 mol of the condensate of 9.2 mols of ethylene oxide with 1 mol of triethanolamine was prepared and then heated at 140°C. for 25 to 30 minutes. This yielded a clear, tough, resinous product.

EXAMPLE XIX

30 40.7 Parts of the condensate of 11.98 mols of ethylene oxide with 1 mol of glycerine was reacted with 34.3 parts of meta-toluylene diisocyanate containing 0.24% of hydrolysable chlorine, the reaction being executed in the presence of 75 parts of chlorinated diphenyl containing 54% chlorine. The product of this reaction was heated at 110°C. for 115 hours and a clear resin was obtained. A sample of this resin was held in the flame until it was burning well and then it was withdrawn. On being withdrawn, the product ceased to burn.

EXAMPLE XX

244 Parts of the condensate of 11.98 mols of ethylene oxide with 1 mol of glycerine was reacted with 205.3 parts of meta-toluylene diisocyanate containing 0.24% of hydrolysable chlorine, the reaction taking place at room temperature and in the presence of 450 parts of chlorinated diphenyl containing 42% of chlorine. This reaction yielded a product which, on heating at 110°C. for a period of 68 hours, produced a completely bubble-free, clear, flexible and tough resin.

55 A sample of the product of the initial reaction was used to impregnate and another to laminate glass cloth with highly satisfactory results. In producing these products, the solution of the initial reaction product was applied to a sheet of cloth and also between two sheets of cloth and then heated to effect polymerisation of the adduct.

EXAMPLE XXI

6.8 Parts of the condensate of 11.98 mols of ethylene oxide with 1 mol of glycerine was reacted with 8.2 parts of p,p'-diisocyanato-diphenylmethane in the presence of 15 parts of chlorinated diphenyl containing 42% of chlorine, the reaction taking place at room temperature. The isocyanate used in this reaction was pretreated with hydrogen chloride to ensure the presence of a trace of hydrogen chloride. The product of this reaction was a very viscous, sticky liquid which, on heating at a temperature of 125°C. for 15 hours, yielded a flexible, clear resin substantially free from bubbles.

Manufacture of Resinous Foams

EXAMPLE XXII.

66.2 Parts of castor oil was dissolved in 100 parts of chlorinated diphenyl containing 54% chlorine by heating and to the resulting solution 33.8 parts of meta-toluylene diisocyanate and 5 parts of N-methylmorpholine were successively added. After the formation of the adduct had been completed, 1% of N-methylmorpholine and 0.4% of benzyltrimethylammonium hydroxide were introduced with stirring. The ensuing reaction, which was carried out at room temperature, resulted in the production of a resinous foam. This product was given an additional cure by heating for 15 minutes at about 100°C. and a light coloured rubbery foam of substantially uniform cell size was obtained.

EXAMPLE XXIII

The preceding example was repeated using hydrogenated instead of natural castor oil. This resulted in the production of a light coloured rubbery foam which was slightly firmer than that obtained in the previous example.

In the production of cellular products of plastic foam, the curing may be effected, as explained in specification No. 773,897, at room temperature by mixing the solution of the initial condensation product with a relatively small proportion of a catalyst which comprises an oxide, hydroxide or alcoholate of an alkali metal or a quaternary ammonium base. However, the rate of curing may be greatly accelerated by heating the solid or liquid solution to higher temperatures as set forth herein. The curing may be carried out in the absence or presence of moisture.

The products of this invention are suitable for casting or pouring into intricate forms or crevices and are adapted for use in numerous applications; for example, as adhesives, protective coatings, components of insulating varnishes, impregnants for fibrous material to impart water resistance, flame resistance and improved bond thereto; as insulating and dielectric elements in transformers, capacitors,

electrical terminals or bushings, cables or other electric devices; and as foamed-in-place resins.

By relatively stable initial condensation product we mean that the product is stable for considerable periods of time if stored at room temperature in tightly closed containers.

WHAT WE CLAIM IS:—

1. A process for the production of a substantially bubble-free plasticised urethane or thiourethane condensation polymer which comprises reacting an excess of an organic polyisocyanate or polyisothiocyanate with an organic polyhydroxy or polymercapto compound in the presence of a non-reactive organic compound so as to form a solid or viscous liquid solution in the non-reactive organic compound of a relatively stable initial condensation product containing at least one urethane or thiourethane group and also at least one free isocyanate or isothiocyanate group and thereafter heating the said solution in the substantial absence of moisture or other added reactive material to form said condensation polymer, said non-reactive compound having a boiling point of at least 200°C. at atmospheric pressure and being soluble in the initial condensation product and the condensation polymer.
2. A process according to claim 1 in which the organic compound is present in an amount of 40—60% of the total weight.
3. A process according to either of the preceding claims in which the solution of the initial condensation product is heated at 60—200°C.
4. A process according to claim 3 in which the solution is heated at 100—125°C.
5. A process according to any of the preceding claims in which the ratio of isocyanate

or isothiocyanate groups to reactive hydrogen atoms present in forming the initial condensation product is at least 1.5 to 1.

6. A process for the production of a plasticised urethane or thiourethane condensation polymer foam which comprises reacting an excess of an organic polyisocyanate or polyisothiocyanate with an organic polyhydroxy or polymercapto compound in the presence of a non-reactive organic compound so as to form a solid or viscous liquid solution in the non-reactive organic compound of a relatively stable substantially bubble-free initial condensation product containing at least one urethane or thiourethane group and also at least one free isocyanate or isothiocyanate group and thereafter treating the said solution with a compound capable of yielding in aqueous solution ionisable hydroxyl or substituted hydroxyl groups or a precursor thereof to form said condensation polymer foam, said non-reactive organic compound having a boiling point of at least 200°C. at atmospheric pressure and being soluble in the initial condensation product and the condensation polymer.

7. A process for the production of a plasticised urethane or thiourethane condensation polymer according to claim 1 or claim 6 and substantially as hereinbefore described with reference to any one of the Examples.

8. A plasticised urethane or thiourethane condensation polymer whenever produced by the process according to any of the preceding claims.

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Chartered Patent Agents,
Agents for the Applicants.

Monsanto Chemical Company

Date of Patent. 6 August 1954

Date of Sealing 17 DECEMBER 1983

(see Sections 53, 57 and 49 of the Patents Act, 1949.)

Note.—The continuance of this Patent is conditional on the payment (by way of Patents Form No. 24) of the prescribed fees which, under The Patents Rules, 1958, are :—

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PLAINTIFF'S EXHIBIT 12

**Australian Patent No. 205456, James H. Saunders and
Herbert L. Heiss**

Pages 756a to 774a

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205456

COMMONWEALTH OF AUSTRALIA.

PATENT SPECIFICATION

Complete Specification Lodged 5th August, 1954.

Application Lodged No. 2193/54 5th August, 1954.

Applicant Monsanto Chemical Company.

Actual Inventors James Henry Saunders and Herbert Louis Heiss.

Convention Application.

(United States of America, 7th August, 1953)

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Classification 09. 4; 47. 7.

No drawing.

COMPLETE SPECIFICATION.

"RESINS PRODUCED FROM URETHANES OR THIOURETHANES AND
METHOD OF PREPARATION."

The following statement is a full description of this invention,
including the best method of performing it known to us:-

The present invention relates to a new series of resins and to
the method of preparing such products.

The products of this invention are suitable for casing or pouring
into intricate forms or crevices and are adapted for use in numerous
applications, for example, as adhesives, protective coatings, components
of insulating varnishes, impregnants for fibrous material to impart water
resistance, flame resistance and improved hand thereto; as insulating
and dielectric elements in transformers, capacitors, electrical terminals
or bushings, cables or other electric devices; and as foamed-in-place
resins. The products of relatively low molecular weight, that is, those
derived from monoamines, monohydroxy compounds or monomercaptans,
find use as plasticizers for vinyl resins and numerous other plastic mat-
erials.

1.

2. 14/2/57 - 110.

In accordance with the present invention, the new products are obtained by reacting an organic compound containing a plurality of groups selected from urethane and thiourethane groups, with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane or thiourethane groups, X is selected from the group consisting of oxygen and sulfur and n is an integer having a value of at least 2, said second mentioned reactant being employed in an amount sufficient to react with at least two of said groups per mol of said first-mentioned reactant and said reaction being carried out in the presence of a non-reactive organic liquid which boils at a temperature not less than about 200°C . at atmospheric pressure.

Thus, the invention provides the method of producing new resinous products which comprises reacting, in the presence of a non-reactive organic liquid boiling at a temperature of at least 200°C . at atmospheric pressure, an organic compound containing a plurality of groups selected from urethane and thiourethane groups, with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane or thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two of said groups per mol of said first-mentioned reactant.

More particularly, the invention provides as a new composition of matter, the cellular product obtained by reacting an organic compound containing a plurality of groups selected from urethane and thiourethane groups, with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane or thiourethane groups, X is selected from the groups consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two of said groups per mol of said first-mentioned reactant and said reaction being carried out in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl and substituted hydroxyl groups and precursors of said compounds, and in the presence of a non-reactive organic liquid having a boiling point of at least 200°C . at atmospheric pressure. The cellular products defined are produced by the method defined above except that the reaction is carried out in the presence of a catalyst selected from the group consisting of compounds yielding an aqueous solution ionizable hydroxyl and substituted hydroxyl groups and precursors of said compounds.

The organic compounds containing a plurality of urethane or

thiourethane groups may be prepared in any suitable manner. For example, compounds containing urethane groups are prepared by reacting an organic hydroxy compound, preferably an organic polyhydroxy compound, with polyisocyanates, carbamyl halides such as carbamyl chloride, urea or substituted ureas; or by reacting mono- or polyamines with halocarbonates such as chlorocarbonates. Compounds containing thiourethane groups are prepared by reacting polyisocyanates with mercaptans or polymercapto compounds.

As illustrative examples of suitable hydroxy compounds for use in the production of organic compounds containing urethane groups, there may be mentioned methyl alcohol, ethyl alcohol, propyl alcohol, iso-propyl alcohol, butyl alcohol, amyl alcohol, hexyl alcohol, octyl alcohol, decyl alcohol, lauryl alcohol, allyl alcohol, oleyl alcohol, tridecyl alcohol, stearyl alcohol, methyl ricinoleate, ethyl lactate, diglycerides, mono-esters of glycols, phenols, substituted phenols, alkylene oxide condensates of these hydroxy compounds, ethylene-glycol, propylene glycol, butylene glycol-2, 3, butylene glycol-1, 3, 2-methyl pentanediol-2, 4, 2-ethylhexane-diol-1, 3, hexamethylene glycol, styrene glycol, N-phenyl-diethanolamine, catechol, resorcinol, 2, 2-bis(4-hydroxyphenyl)propane, p, p'-dihydroxybiphenyl, decamethylene glycol; polyglycols (ether glycols) such as polyethylene glycols, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycols 200, 400 and 600; polypropylene glycols, dipropylene glycol, tripropylene glycol, polypropylene glycols 400, 750, 1200 and 2000; Carbowaxes 1000, 1000 W, 1500; monoethers of tri-hydroxy compounds such as glycetyl-a-allyl ether, glycetyl-a-phenyl ether, glycetyl-a-isopropyl ether; hydroxy esters such as an ester prepared from 1 mol of dibasic acid and 2 mols of a glycol or polyglycol, a polyester prepared so that the molar ratio of glycol or polyglycol to the dibasic acid is between 2 and 1, an ester prepared from 1 mol of a dimer acid and 2 mols of a glycol or polyglycol, an ester prepared from a hydroxy acid and a glycol or polyglycol so that the molar ratio of the glycol or polyglycol to the hydroxy acid is between 0.5 and 1 and an ester prepared from 1 mol of a trihydroxy compound and 1 mol of a monobasic acid, such as the monoglyceride of eleostearic acid; trihydroxy compounds such as glycerine, triethanolamine, pyrogallol, phloroglucinol, and the like, alkylene oxide condensates of glycerine, triethanolamine, pyrogallol, phloroglucinol, and the like; monoethers of tetrahydroxy compounds; esters prepared from hydroxy acid and a trihydroxy compound so that the molar ratio of the latter to the former is between 0.33 and 1, such as glycerine triricinoleate, esters prepared from 1 mol of a monobasic acid and 1 mol of a tetrahydroxy

compound; tetrahydroxy compounds such as pentaerythritol, and the like, alkylene oxide condensates of pentaerythritol, and the like, esters prepared from 1 mol of a dibasic acid and 2 mols of a trihydroxy compound; pentahydroxy compounds, such as arabitol, xylitol, and the like; hexahydroxy compounds such as sorbitol, ducitol and mannitol, and the like.

Examples of suitable compounds which may be reacted with polyisocyanates to form thiourethanes are methyl mercaptan, ethyl mercaptan, butyl mercaptan, octyl mercaptan, cyclohexyl mercaptan, octadecyl mercaptan, allyl mercaptan, phenyl mercaptan, tolyl mercaptan, *a*-naphthyl mercaptan, dimercaptoethane, 1, 2, 3-trimercaptopropane, 1, 2, 3-trimercaptobutane, 1, 5-dimercapto-3-(mercaptopropyl)pentane, 1, 6-dimercaptohexane, 1, 10-dimercaptodecane, 1, 6-dimercapto-3-methylhexane, 1, 4-dimercaptobenzene, dimercaptoxylylene, and polyvinyl mercaptan.

Illustrative examples of suitable isocyanates, isothiocyanates, carbamyl chlorides, and ureas which may be employed in the production of organic compounds containing urethane or thiourethane groups are ethyl, methyl, propyl, butyl, amyl, octyl, decyl, dodecyl, hexadecyl, octadecyl, allyl, isobutyl, isoamyl, cyclohexyl, phenyl, *p*-tolyl, *p*-chlorophenyl, *m*-chlorophenyl and *a*-naphthyl isocyanates, and the like; ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, and the like; and the corresponding diisothiocyanates; alkylene diisocyanates and diisothiocyanates, such as propylene-1, 2-diisocyanate, butylene-1, 2-diisocyanate, butylene-1, 3-diisocyanate, butylene-2, 3-diisocyanate, and butylene-1, 3-diisothiocyanate; alkylidene diisocyanates and diisothiocyanates, such as ethylidene diisocyanate, butylidene diisocyanate and ethylidene diisothiocyanate; cycloalkylene diisocyanates and diisothiocyanates, such as cyclopentylene-1, 3-diisocyanate, cyclohexylene-1, 2-diisocyanate, cyclohexylene-1, 3-diisocyanate, cyclohexylene-1, 4-diisocyanate, and cyclohexylene-1, 2-diisothiocyanate; cycloalkylidene diisocyanates and diisothiocyanates, such as cyclopentylidene diisocyanate, cyclohexylidene diisocyanate and cyclohexylidene diisothiocyanate; aromatic diisocyanates and diisothiocyanates, such as *m*-phenylene diisocyanate, *p*-phenylene diisocyanate, 1-methyl-2, 4-phenylene diisocyanate, naphthylene-1, 4-diisocyanate, diphenylene-4, 4'-diisocyanate or *p*-phenylene diisothiocyanate; aliphatic-aromatic diisocyanates or diisothiocyanates, such as xylidine-1, 4-diisocyanate, xylidine-1, 3-diisocyanate, 4, 4'-diphenylmethane diisocyanate, 4, 4'-diphenylpropane diisocyanate or xylidine-1, 4-diisothiocyanate; methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, phenyl, cyclohexyl, *p*-chlorophenyl carbamyl chlorides; *m*-phenylene, *p*-phenylene, 2, 4-tolylene, 4, 4'-xylene bis-carbamyl chlorides; urea, methylurea, ethyl-

urea, butylurea, phenylurea, *a*-naphthylurea, cyclohexylurea, s-dimethylurea, s-dicyclohexylurea, s-diphenylurea, 1,3-methylethylurea and 1,3-ethylphenylurea, and the like.

Examples of amines which may be used in the preparation of organic compounds containing urethane groups are: methyl, ethyl, butyl, octyl, cyclohexyl, octadecyl, allyl amines, aniline, p-toluidine, substituted anilines and *a*-naphthylamine; ethylene diamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine, octamethylene diamine, decamethylene diamine, dodecamethylene diamine, N,N'-dimethyl decamethylene diamine, N,N'-dibenzyl hexamethylene diamine, cyclohexylene-1-4-diamine, ortho-phenylene diamine, -m-phenylene diamine, p-phenylene diamine, benzidine, naphthalene-1,4-diamine, γ , γ' -diamino dibutyl oxide, γ , γ' -diamino dibutyl sulfide, diethylene triamine and triethylene tetramine, and the like.

As typical examples of halocarbonates which may be reacted with amines to form organic compounds containing urethane groups, there may be mentioned, methyl, ethyl, propyl, isopropyl, butyl, cyclohexyl, phenyl, p-tolyl and p-chlorophenyl chlorocarbonates and butylene-1,4- and hexylene-1,6- bis-chlorocarbonates, and the like.

The organic compounds containing urethane and/or thiourethane groups used in the practice of the instant invention are preferably prepared by reacting an organic compound of the general formula: R(NCX)_n with an organic polyhydroxy and/or polymercapto compound in the proportions providing a ratio of -NCX groups to active hydrogen atoms which is greater than 1:1 but is desirably within the range of 1.1:1 to n:1. More specifically, these reactants are employed in the proportions providing a ratio of -NCX groups to active hydrogen atoms which falls in the range of about 1.3:1 or 1.5:1 to about n:1 and preferably within the range of about 2:1 to about n:1. The products obtained by this reaction are adducts which contain urethane and/or thiourethane groups and also free isocyanate and/or isothiocyanate groups. Therefore, these products can be converted into more highly polymerized products by bringing out a reaction between the isocyanate and/or isothiocyanate groups of one molecule with the urethane and/or thiourethane groups of the same or another molecule. This is achieved by heating the adducts in the substantial absence of moisture or by means of catalysts. Alternatively, the organic compounds containing urethane and/or thiourethane groups and also isocyanate and/or isothiocyanate groups may be converted into a more highly polymerized state by further reaction with a polyisocyanate and/or polyisothiocyanate.

The products of the instant invention may be in the form of bubble-

free resinous compositions or highly cellular resinous foams, the character of the products being dependent upon the conditions of manufacture.

For example, if a substantially bubble-free resin is desired, the reaction between the organic compound containing urethane and/or thiourethane groups with a polyisocyanate and/or polyisothiocyanate is desirably carried out in the absence of a catalyst and also moisture. On the other hand, if a cellular product is desired, the reaction is effected in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl or substituted hydroxyl groups and precursors of said compounds. In either case, the products, which otherwise are relatively brittle resins, are plasticized and rendered more flexible by effecting their preparation in the presence of the non-reactive organic organic liquid which boils at a temperature not lower than 200°C., and preferably not lower than 250°C., at atmospheric pressure.

As illustrative examples of non-reactive organic liquids which may be used in the practice of this invention, there may be mentioned trichlorobenzene, chlorinated biphenyl, chlorinated, 1, 3, 3-trimethyl-1-phenylindane, chlorinated 1, 3, 3, 6-tetramethyl-1(4'-methyl-phenyl)indane, dimethoxy tetraethylene glycol, diethyl phthalate, dibutyl phthalate, diethyl phthalate, butyl benzoyl benzoate, butyl phthalyl butyl glycolate, N-ethylpara-toluene sulfonamide, diphenyl ortho-biphenyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, dibutyl sebacate, dibenzyl sebacate, partially hydrogenated aromatic hydrocarbon liquid mixtures such as disclosed and claimed in U. S. patent No: 2, 364, 719, epoxidized safflower oil and petroleum and coal tar oils which boil above 200°C., and preferably above 250°C., at atmospheric pressure. In fact any organic liquid boiling within the above range which is compatible with the above adducts, the organic compounds containing urethane groups and the final resin are employed in the practice of the instant invention.

The above-described adducts may be preformed and then added to the non-reactive organic liquid or solid and converted to a more highly polymerized state or they may be formed in situ in the organic liquid or solid and then converted to a higher state of polymerization. In either event, the plasticized polymers thus obtained vary from soft resinous gels to hard brittle resins, depending upon the amount and type of components used in their production.

For a more complete understanding of the instant invention, reference is made to the following illustrative examples, in which and throughout this description the parts mentioned are by weight unless otherwise specified, although it should be clearly understood that the invention

is not limited thereto.

EXAMPLE I. Manufacture of Substantially Bubble-Free Gels and Resins. About 11.1 parts of triethanolamine was reacted with about 38.9 parts of m-tolylene diisocyanate in the presence of about 50 parts of chlorinated biphenyl containing 42% chlorine. The resulting mixture consisted of a white solid suspended in a yellow liquid. This liquid was separated and heated in an oven at a temperature of 100°C. for about 12 hours and a hard, clear resin was obtained.

A sample of this resin was held in a Bunsen flame and it burned with a smokey flame without melting but extinguished itself as soon as it was removed.

EXAMPLE II. About 55.5 parts of triethanolamine and about 250 parts of chlorinated biphenyl containing 42% chlorine were mixed thoroughly in a flask and then about 194.5 parts of m-tolylene diisocyanate was added with stirring. During this addition, the reaction temperature was maintained at a value not exceeding 50°C. This resulted in the production of a slurry of a solid material which was separated from the liquid by filtering. A sample of the liquid reaction product was placed in an oven at 100°C. and, after about 18 hours, the liquid solidified. The solubility of this product in various liquids was determined and it was found that the resin did not dissolve in boiling solvents such as water, methanol, acetone, hexane, benzene, carbon tetrachloride and ethyl acetate.

EXAMPLE III. A slurry containing about 39.1 parts of diethanolamine and about 250 parts of chlorinated biphenyl containing 42% chlorine was reacted with about 194.5 parts of m-tolylene diisocyanate to form a liquid product containing a relatively small proportion of solid material which was separated by filtering. The liquid product was then heated in an oven at 100°C. until it solidified into a hard, clear resin.

EXAMPLE IV. About 38.9 parts of m-tolylene diisocyanate and about 11.1 parts of triethanolamine were reacted together in the presence of about 50 parts of nuclear chlorinated isopropylbiphenyl containing about 42% chlorine. The reaction product consisted of a liquid containing a relatively small proportion of solids which were removed by filtration. The liquid portion of the reaction product was heated in an oven at 100°C. for a period of about 24 hours and a soft, yellow resinous gel was obtained.

EXAMPLE V. About 11.1 parts of triethanolamine and about 38.9 parts of m-tolylene diisocyanate were reacted together in the presence of about 50 parts of the following solvents:

-
- Sample No. 1 Chlorinated biphenyl containing 21% chlorine
Sample No. 2 Chlorinated biphenyl containing 32% chlorine
Sample No. 3 Chlorinated biphenyl containing 42% chlorine
Sample No. 4 Chlorinated biphenyl containing 48% chlorine
Sample No. 5 Chlorinated biphenyl containing 54% chlorine
Sample No. 6 Chlorinated biphenyl containing 60% chlorine
Sample No. 7 Chlorinated naphthalene.

On heating to a temperature of 100°C. and for a period of about 20 hours, Sample Nos. 1-5 and 7 formed clear, amber resins whereas Sample No. 6 produced a sticky, opaque resin.

EXAMPLE VI. About 55.5 parts of triethanolamine and about 194.5 parts of m-tolylene diisocyanate were reacted together in the presence of about 250 parts of chlorinated biphenyl containing 42% chlorine. This reaction was carried out at room temperature using chlorinated biphenyl which had been previously saturated with hydrogen chloride gas. This resulted in the production of a liquid containing a relatively small proportion of solids which were removed by filtration. A sample of this liquid product was heated at a temperature of 100°C. for about 3 1/4 hours to form a thick gel and for a total of about 4 1/4 hours to form a very hard and brittle resin which was substantially free of bubbles.

EXAMPLE VII. About 8.3 parts of triethanolamine and about 41.7 parts of p, p'-diisocyanatodiphenylmethane were reacted together in the presence of about 50 parts of chlorinated biphenyl containing about 42% chlorine. The resulting reaction product was placed in a 100°C. oven and heated for about 5 hours. This resulted in the production of a hard, clear, yellow resin similar to that obtained with m-tolylene diisocyanate.

EXAMPLE VIII. About 11.1 parts of triethanolamine was dissolved in about 50 parts of molten biphenyl and to the resulting solution about 38.9 parts of m-tolylene diisocyanate was added. The product obtained as a result of the ensuing reaction was heated for about 24 hours at 100°C. and a hard, clear, light yellow resin was obtained.

EXAMPLE IX. About 10.3 parts of castor oil was reacted with about 4.7 parts of m-tolylene diisocyanate in the presence of chlorinated biphenyl containing 42% chlorine, the reaction taking place at room temperature. The product of this reaction was a clear, viscous liquid which, on heating for about 40 hours at 125°C., yielded a flexible, bubble-free resin.

EXAMPLE X. m-Tolylene diisocyanate and the condensate of about 6.6 mols of propylene oxide with 1 mol of glycerine were reacted together in a molar ratio of about 3 mols of the diisocyanate to about 1 mol of the condensate, the reaction taking place in the presence of a suff-

icient amount of chlorinated biphenyl containing 42% chlorine to yield a 50% solution of adduct. On heating for 2 1/4 hours at 140°C., a sample of this solution yielded a tough, rubbery and resinous gel.

EXAMPLE XI. m-Tolylene diisocyanate containing about .23% hydrolyzable chlorine was reacted with the following alkylene oxide condensates of glycerine in a molar ratio of about 3 mols of the isocyanate to about 1 mol of the condensate, the reaction taking place in the presence of sufficient amount of chlorinated biphenyl containing 42% chlorine to yield a 50% solution of the adduct.

Condensate of about 3.1 mols of propylene oxide
with 1 mol of glycerine

Condensate of about 13.2 mols of propylene oxide
with 1 mol of glycerine

Condensate of about 12 mols of ethylene oxide with
1 mol of glycerine

Condensate of about 3 mols of ethylene oxide with
1 mol of glycerine

The products of these reactions were all clear, viscous liquids except the solution of adduct prepared from 3:1 mols of propylene oxide with 1 mol of glycerine, which product was a cloudy, viscous liquid. On being heated to 150°C. for 3 hours, 4 3/4 hours, 7 1/2 hours and 4 3/4 hours, respectively, these reaction products formed gels which, on continued heating for a total of 23 hours at the same temperature, produced flexible, bubble-free resins that decreased in flexibility with decreasing molecular weight of the condensate used in the preparation of the adduct.

EXAMPLE XII. Solutions of the following compositions, when heated for about 23 hours at 125°C., yielded substantially bubble-free products which varied with decreasing amounts of solvent from a soft jelly to a tough, flexible resin.

<u>Adduct</u>	<u>% By Weight Of Adduct</u>	<u>% By Weight of Chlorinated Biphenyl Containing 42% Chlorine</u>
Adduct of about 3 mols of <u>m</u> -tolylene diisocyan- ate with about 1 mol of the condensate of 13.2 mols of propylene oxide with 1 mol of glycerine	20	80
"	35	65
"	65	35
"	80	20

EXAMPLE XIII. Solutions of the following compositions, when heated for about 23 hours at 125°C. produced substantially bubble-free, brittle resins which increased in hardness as the amount of solvent was decreased.

<u>Adduct</u>	<u>% By Weight Of Adduct</u>	<u>% By Weight of Chlorinated Biphenyl Containing 42% Chlorine</u>
Adduct of 3 mols of <u>m</u> -tolylene diisocyanate with 1 mol of the condensate of 3.1 mols of propylene oxide with 1 mol of glycerine	20	80
"	35	65
"	65	35
"	80	20

EXAMPLE XIV Substantially 3 mols of m-tolylene diisocyanate was reacted with the condensation product of about 13.2 mols of propylene oxide with 1 mol of glycerine in the presence of a sufficient amount of the following chlorinated compounds numbered 1-6, inclusive, to yield a 50% solution of the resulting adducts. In the remaining cases, namely, 7-9, inclusive, the condensation product was mixed with similar amounts of the melted chlorinated compound and then reacted with the m-tolylene diisocyanate.

	<u>Physical Appearance of Adduct.</u>		
1. Unrefined chlorinated biphenyl containing 48% by weight of chlorine	Dark liquid		
2. Chlorinated biphenyl containing 21% chlorine	Clear, viscous liquid		
3. Chlorinated biphenyl containing 32% chlorine	" " "		
4. Refined chlorinated biphenyl containing 48% chlorine	" " "		
5. Refined chlorinated biphenyl containing 54% chlorine	" " "		
6. Refined chlorinated biphenyl containing 60% chlorine	Very viscous, clear liquid		

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Physical Appearance of
Adduct

7.	Chlorinated mixture of 60% biphenyl and 40% distilled high boiler containing 65% chlorine	Clear, extremely viscous liquid
8.	Chlorinated isomeric terphenyl mixture containing 42% chlorine	Clear, extremely viscous liquid
9.	Chlorinated distilled high boiler containing 60% chlorine	Clear solid

The products obtained as a result of these reactions were heated at a temperature of 125°C. until a gel was formed, whereupon the heating was continued for a total of 13 hours to convert the gel into a resin. The time required to gel the above products and the type of resins formed are indicated in the following table.

<u>Sample No.</u>	<u>Total Time Required For Sample to Gel.</u>	<u>Type of Resin Formed</u>
1	Greater than 6 hours	Dark, flexible, soft, bubble-free resin
2	2 1/2 hours	Flexible, bubble-free resin
3	1 1/2 hours	Flexible, bubble-free resin
4	1 1/2 hours	Flexible, bubble-free resin
5	Greater than 6 hours	Soft, flexible, bubble-free resin
6	Greater than 6 hours	Soft, flexible resin with a few bubbles
7.	1 1/2 hours	Hard, flexible, bubble-free resin
8.	2 1/2 hours	Flexible, bubble-free resin
9	2 1/2 hours	Brittle resin with a few bubbles

EXAMPLE XV. Substantially 3 mols of m-tolylene diisocyanate was reacted with about 1 mol of the condensation product of about 13.3 mols of propylene oxide with 1 mol of glycerine, the reaction taking place in the presence of a sufficient amount of the following organic liquids to form a 50% solution of the adduct having the properties indicated:

<u>Sample No.</u>	<u>Physical Properties Of Solution of Adduct</u>
1	Partially hydrogenated aromatic liquid mixture having a specific gravity of about 1.004 at 25°C., a refractive index of about 1.5600 at 25°C. and a boiling range of 340°C. to 390°C. at atmospheric pressure
2	Chlorinated 1:3:3-trimethyl-1-phenyl-indane.
3	Epoxidized safflower oil
4	Tricresyl phosphate
5	2-ethylhexyl diphenyl phosphate
6	Butyl phthalyl butyl glycolate
7	Dimethoxy tetraethylene glycol
	Clear liquid

The above products were heated at a temperature of about 125°C until they were gelled and then the gels were heated up to a total of 22 1/2 hours to convert them into resins. The time required for the products to gel and the properties of the resins are given in the following table.

	<u>Time Required for Sample to Gel. Hrs.</u>	<u>Type of Resin Formed</u>
1	Greater than 6 1/2	Flexible resin with some tendency of organic liquid to exude
2	3 1/2	Flexible resin
3	1	" "
4	5 1/2	" "
5	3	" "
6	5 1/2	" "
7	More than 2 1/2	" "

EXAMPLE XVI About 3 mols of m-tolylene diisocyanate was reacted with about 1 mol of the condensate of 13.2 mols of propylene oxide with 1 mol of glycerine, the reaction being executed in the presence of containing 42% chlorine to yield 20%, 50% and 80% solutions of the adduct. A similar reaction was carried out using about 3 mols of m-tolylene diisocyanate and about 1 mol of the condensate of 3.1 mols of propylene oxide with 1 mol of glycerine. The resulting reaction products were further heated to yield resinous polymers plasticized by the solvent employed.

Similar products were also made by adding the above condensates to the following molten chlorinated compounds, reacting m-tolylene diisocyanate with the condensate in the molar ratio indicated above and then heating the resulting products to convert them into plasticized resinous polymers.

1. A chlorinated mixture consisting of 60% biphenyl and 40% distilled high boiler containing about 65% chlorine
2. A chlorinated isomeric terphenyl mixture containing 42% chlorine
3. Chlorinated distilled high boiler containing about 60% chlorine

In order to determine the temperature characteristics of these resins, they were cooled to -12°C. and heated to 200°C. and 300°C. on a Fisher-Johns melting point apparatus. All of these resins were liquid or extremely soft at 300°C. and gave off vapor. At 200°C. very little change in the nature of the resins was noted, but at -12°C., all of these resins were quite brittle.

EXAMPLE XVII. About 8 parts of the condensate of 13.2 mols of propylene oxide with 1 mol of glycerine was reacted with about 7 parts of p,p'-diisocyanatodiphenylmethane which had been pretreated with HCl gas, the reaction being executed in the presence of 15 parts of chlorinated biphenyl containing about 42% chlorine. The product of this reaction was a soft, sticky, gummy, cloudy liquid. A sample of this product was heated at 125°C. for a period of about 15 hours and a clear, flexible resin substantially free of bubbles was obtained.

EXAMPLE XVIII A mixture of about 15 parts of chlorinated biphenyl containing 42% chlorine and about 15 parts of the adduct of about 3 mols of m-tolylene diisocyanate with about 1 mol of the condensate of 9.2 mols of ethylene oxide with 1 mol of triethanolamine was prepared and then heated at 140°C. for about 25 to 30 minutes. This yielded a clear, tough, resinous product.

EXAMPLE XIV About 40.7 parts of the condensate of

11.98 mols of ethylene oxide with 1 mol of glycerine was reacted with about 34.3 parts of m-tolylene diisocyanate containing 0.24% hydrolyzable chlorine, the reaction being executed in the presence of about 75 parts of chlorinated biphenyl containing 54% chlorine. The product of this reaction was heated at 110°C. for about 115 hours and a clear resin was obtained. A sample of this resin was held in the flame until it was burning well and then it was withdrawn. On being withdrawn, the product did not continue to burn.

EXAMPLE XX. About 244 parts of the condensate of 11.98 mols of ethylene oxide with 1 mol of glycerine was reacted with about 205.3 parts of m-tolylene diisocyanate containing 0.24% of hydrolyzable chlorine, the reaction taking place at room temperature and in the presence of about 450 parts of chlorinated biphenyl containing 42% chlorine. This reaction yielded a product which, on heating at about 110°C. for a period of about 68 hours, produced a completely bubble-free, clear, flexible and tough resin.

A sample of the product of the initial reaction was used to impregnate and/or laminate glass cloth with highly satisfactory results. In producing these products, the solution of the initial reaction product was applied to a sheet of cloth and also between two sheets of cloth and then heated to effect polymerization of the adduct.

EXAMPLE XXI About 6.8 parts of the condensate of 11.98 mols of ethylene oxide with 1 mol of glycerine was reacted with about 8.2 parts of p,p'-diisocyanatodiphenylmethane in the presence of about 15 parts of chlorinated biphenyl containing 42% chlorine, the reaction taking place at room temperature. The isocyanate used in this reaction was pretreated with hydrogen chloride to insure the presence of a trace of HC1. The product of this reaction was a very viscous, sticky liquid which, on heating at a temperature of about 125°C. for about 15 hours, yielded a flexible, clear resin substantially free of bubbles.

EXAMPLE XXII Manufacture of Resinous Foams. The procedure described in Example X was repeated except that 1% by weight of calcium oxide was added to a sample of the resulting solution of adduct. On heating this sample at 140°C. for 10 minutes, it was converted initially into a gel and finally into a porous resinous foam.

EXAMPLE XXIII The procedure used in Example XI was repeated using m-tolylene diisocyanate which had been pretreated with hydrogen chloride, and a condensate of about 3 mols of propene oxide with 1 mol of glycerine to form a 50% solution of adduct. A sample of this solution was mixed with about 1% by weight of lead oxide and the resulting mixture heated at 140°C. for about 1 1/4 to 1 3/4 hours. This

resulted in the production of a rubbery, resinous foam.

EXAMPLE XXIV About 66.2 parts of castor oil was dissolved in about 100 parts of chlorinated biphenyl containing 54% chlorine by heating and to the resulting solution about 33.8 parts of m-tolylene di-isocyanate and about 5 parts of N-methylmorpholine were successively added. After the formation of the adduct had been completed, about 1% of N-methylmorpholine and about 0.4% of benzyltrimethylammonium hydroxide were introduced with stirring. The ensuing reaction, which was carried out at room temperature, resulted in the production of a resinous foam. This product was given an additional cure by heating for 15 minutes at about 100°C. and a light colored rubbery foam of substantially uniform cell size was obtained.

EXAMPLE XXV. The preceding example was repeated using hydrogenated instead of natural castor oil. This resulted in the production of a light colored rubbery foam which was slightly firmer than that obtained in the previous example.

The organic compound containing a urethane or thiourethane group or one or more of these groups and an isocyanate and/or an isothiocyanate group is prepared in the presence of the non-reactive organic liquid plasticizer, which boils at a temperature of at least 200°C. and preferably at a temperature of at least 250°C. at atmospheric pressure. This yields a solid or a viscous liquid solution of the above organic compound, which is stable for a considerable period of time if stored at room temperature in tightly closed containers. However, if heated or treated in the manner hereinafter described, the solution is converted into a complex resinous polymer plasticized by the above-mentioned plasticizer.

The curing of the solid or viscous liquid solution of the above-mentioned organic compound is effected by heating in the substantial absence of moisture or other foreign materials containing reactive hydrogen atoms. This heating is sufficient to effect a reaction between the urethane or thiourethane group and an isocyanate and/or an isothiocyanate group of another molecule containing both types of functional groups. In the event that the organic compound contains only urethane or thiourethane groups, then it is cured by reaction with an added compound which contains at least one isocyanate and/or isothiocyanate group, the curing taking place at a temperature sufficient to bring about a reaction between the functional groups of the two compounds involved.

The curing operation is carried out in the absence or presence of a catalyst and at a temperature varying from room temperature up to about 225°C. or more specifically, from about 60°C. to about 200°C.

and within these limits, a temperature of about 100°C. to about 125°C. is preferred.

In the production of cellular products or plastic foam, the curing is effected at room temperature by mixing the organic material containing the urethane or thiourethane groups as defined with a relatively small proportion of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl or substituted hydroxyl groups and precursors of these compounds. The expression "substituted hydroxyl groups" signified radicals of the formula -OX, in which X is a member selected from the group consisting of aliphatic, cycloaliphatic aryl, alkaryl, aralkyl and substituted hydrocarbon radicals which may or may not be interrupted by non-reactive hetero atoms such as sulfur and oxygen, and the like. For example, these hydrocarbons radicals may be substituted by alkyl, alkoxy, halogen and/or nitro groups. Illustrative examples of preferred catalysts within the group are the oxides or hydroxides of potassium, sodium and calcium; the oxides of magnesium, zinc and lead; the alkali metal salts and particularly the sodium salts of ortho-phenyl phenol, 2, 4, 5-trichlorophenol and 2, 3, 4, 6-tetrachlorophenol; and benzyltrimethylammonium hydroxide, tetramethylammonium hydroxide, tetramethylphenylammonium hydroxide, tetraethylammonium hydroxide, and the like. These catalysts may be used alone or in combination with tertiary organic amines such as N-methylmorpholine, N-ethylmorpholine, triethylamine, tripropylamine, tributylamine, triamylamine, pyridine and quinoline, and the like. If desired, the rate of curing may be treatly accelerated by heating the solid or liquid solution to higher temperatures within the limits set forth above.

In the production of cellular products or plastic foams, the catalyst is employed in an amount varying from about 0.001% to about 5% by weight or more specifically, within the range of about 0.1% to about 3% by weight and within these limits about 0.5% to about 1% is preferred. The percentage by weight is based upon the weight of the total reactants.

In the production of plasticized products in accordance with this invention, the liquid plasticizer is desirably employed in an amount varying from about 20% to about 80% by weight, basis total weight, and within these limits about 40% to about 60% by weight is preferred. If desired, larger or smaller amounts may be employed in order to effect the desired degree of plasticization.

The plasticized products of the instant invention cannot be produced by first forming the polymerized or cured organic compound containing a urethane or thiourethane group and then incorporating the cured product with the plasticizer. In order to obtain products having satisfactory

properties, the organic compound containing the urethane or thiourethane group must be intimately associated with the plasticizer and then polymerized or cured to a higher molecular state. In this operation, the organic compound containing the urethane or thiourethane group may be preformed and then added to the plasticizer or it may be formed in situ.

The claims defining the invention are as follows:-

1. As a new composition of matter, the product obtained by reacting an organic compound containing a plurality of groups selected from urethane and thiourethane groups, with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane or thiourethane groups, X is selected from the group consisting of oxygen and sulfur and n is an integer having a value of at least 2, said second mentioned reactant being employed in an amount sufficient to react with at least two of said groups per mol of said first-mentioned reactant and said reaction being carried out in the presence of a non-reactive organic liquid which boils at a temperature not less than about 200°C. at atmospheric pressure. (Priority date: 7th August, 1953)

2. As a new composition of matter, the cellular product obtained by reacting an organic compound containing a plurality of groups selected from urethane and thiourethane groups, with a compound of the general formula: $R(NCX)_n$, wherein R is an organic radical free from functional groups other than -NCX, urethane or thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two of said groups per mol of said first-mentioned reactant and said reaction being carried out in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl and substituted hydroxyl groups and precursors of said compounds, and in the presence of a non-reactive organic liquid having a boiling point of at least 200°C. at atmospheric pressure. (Priority date: 7th August, 1953)

3. New resinous compositions substantially as described herein. (Priority date: 7th August, 1953)

4. The method of producing a new composition of matter, which comprises reacting, in the presence of a non-reactive organic liquid boiling at a temperature of at least 200°C. at atmospheric pressure,

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an organic compound containing a plurality of groups selected from urethane and thiourethane groups, with a compound of the general formula: R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCX, urethane or thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two of said groups per mol of said first-mentioned reactant. (Priority date: 7th August, 1953)

5. The method of producing, a cellular product, which comprises reacting, in the presence of a non-reactive organic liquid boiling at a temperature of at least 200°C. at atmospheric pressure, an organic compound containing a plurality of groups selected from urethane and thiourethane groups, with a compound of the general formula: R(NCX)_n, wherein R is an organic radical free from functional groups other than -NCX, urethane or thiourethane groups, X is selected from the group consisting of oxygen and sulfur, and n is an integer having a value of at least 2, said second-mentioned reactant being employed in an amount sufficient to react with at least two of said groups per mol of said first-mentioned reactant and said reaction being carried out in the presence of a catalyst selected from the group consisting of compounds yielding in aqueous solution ionizable hydroxyl and substituted hydroxyl groups and precursors of said compounds. (Priority date: 7th August, 1953)

6. The method of producing new resinous compositions substantially as described in anyone of the Examples herein.
(Priority date: 7th August, 1953)

EDWIN F. WELLINGTON.
Patent Attorney for Applicant.

References:

<u>Serial No.</u>	<u>Application No.</u>	<u>Classification</u>
164,975	17,247/53	09.4
166,931	21,782/53	09.4
155,589	9168/52	47.7

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205,456

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PLAINTIFF'S EXHIBIT 13

"More Polyethers Coming", Chemical and Engineering News, Pages 72, 150 (October 14, 1957)

Pages 775a to 776a

CHEMICALS



Edible "instant gel" is tough; it forms when a purified liquid fat is combined with water. William C. Lyman (left), and George Y. Brokaw look at the new gel which may find application in the cosmetic, pharmaceutical, and food industries.

Instant Gel

Researchers report that gel forms in seconds when distilled monoglyceride is mixed with water

EASTMAN KODAK has developed a new nonpetroleum gel that forms almost instantly when a distilled monoglyceride is stirred into water. It forms in one or two seconds after it's mixed with the water.

The new gel was discovered, after three years' work on purification of materials. "Because the gel is formed from highly purified liquid monoglycerides, it is edible and nutritious," according to John C. Hecker, general manager of Kodak's Distillation Products Industries Division. "But its possibilities appear to lie as much in the cosmetic, pharmaceutical, and other fields as in the food industry."

The gel, in a modified form, has been tested successfully as a means of boosting the "whip" in whipped toppings for dessert. This leads Hecker to believe

that the product might give housewives a new kind of whipped dairy product when they mix a crystalline form of the gel with milk. He thinks too that since the liquid monoglyceride gels on moisture contact, it may find use in medicine when it is combined with a liquid medicine. It could also be considered for hair dressings and deodorant creams. In industry, the gel could possibly win a role as a special lubricant or antirust additive, he claims.

George Y. Brokaw and William C. Lyman, both of Kodak's DPI Division, say that when concentrated monoglycerides (such as distilled products) are heated to about their melting point with water, the gel forms. The exact temperature at which the material gels depends on the molecular weight of the fatty acid from which the monogly-

eride is derived and on the purity of the monoglyceride. They point out that monolaurin does not gel but monopalmitin does.

Additives can prevent gelation, they say, with triglycerides showing twice as much effectiveness as diglycerides in doing the job.

Brokaw and Lyman told of the new development at the American Chemists Society meeting in Cincinnati last week.

More Polyethers Coming

Carbide heads for more of the polyurethane raw material market with propylene oxide-hexanetriol adducts

THIS WEEK, Carbide announced its new polyethers—headed for the polyurethane market. During 1957, low price polyethers made strong dent in polyesters' relative share of the urethane foam market.

Carbide's entry is not unexpected (C&EN, Mar. 25, page 96). Its diol 2025, selling in tank cars at 25 cents per pound delivered, is one of the dominant polyethers in today's market. However, it is generally used with cross-linking agents of higher functionality.

The new series is designed to avoid this extra step. Each is a propylene oxide-hexanetriol adduct, with molecular weights ranging from 700 to 4000. Tank car prices are between 27½ and 36 cents per pound. Carbide has come up with a new trademark for its urethane industry intermediates—Nlax. It also will market glycerol adducts of the same molecular weights.

The 4000 and 2500 molecular weight polyethers are intended for soft foams and flexible cushioning. The 1500 polymer can be blended with diols to form cushioning. Perhaps especially significant is the 700 molecular weight material which makes rigid and semi-rigid foams. It can also be used for coating.

Wyandotte Chemicals and Dow are the other two of the big three major polyether suppliers for urethane foams. However, several other companies may be ready to enter the field in a big way.

One of these is Jefferson Chemical who plans to produce propylene oxide. With this, Jefferson is a likely prospect to offer polyethers soon.

(Continued on page 150)

(Situations Wanted, Continued)

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MISCELLANEOUS

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CHEMICALS

(Continued from page 72)

► **Werner G. Smith, Inc.**, is now making a new wax known as Hywax 135. The fatty alcohol ester is heat stable and changes color little when heated to 554° F. Company says stability is partly due to product's low iodine number and high purity. Uses include lubricant for plastics, textile finishes and processing aids, superfatting agent, rust inhibitors, wire-drawing compounds, and lacquers. C 1

► **CPC** is producing and making available methionine sulfone, methionine sulfoxide, α -methyl methionine, oxythiamine HCl, α -ketobutyric acid, 4-ethoxypyrimidone - 2(4-ethoxy - 2-hydroxypyrimidine). C 2

► **Stein, Hall & Co.** is now making a complete line of vinyl pyrrolidone polymers and copolymers. C 3

► A new chelating agent, Sole-onic CH50, is commercially available from Sole Chemical. Sole says the agent is designed to operate in very high pH systems with longer than usual sequestering life. C 4

► **Petronate CR** is a new rust preventive agent made by L. Sonnenborn Sons. Company calls it a universal rust preventive, pointing out that the agent can be used interchangeably with a variety of different carrier oils. C 5

► A new phenolic resin, designated #3725, for use in can linings, is available from Allied Chemical & Dye's Barrett Division. Product is based on a modified phenol, Barrett says, and is oil soluble and nonreactive to heat. C 6

► **FMC Organic Chemicals Division** is making available in development quantities methylallyl alcohol (2-methyl-2-propene-1-ol). The new chemical has use in organic synthesis and in the resin and plastics field. C 7

► **Dow Corning** introduces Silastic RTV 561, a new room-temperature vulcanizing silicone rubber that the company recommends for encapsulating electric and electronic parts and for general potting, sealing, and caulking applications. C 8

► **Citraconic anhydride**, a low molecular weight liquid, is introduced by Chas. Pfizer's commercial development division. The liquid anhydride is available in research and pilot plant quantities. Pfizer says initial testing shows the product is promising in curing epoxy resins, preparing polyester resins and serving as an intermediate. C 9

► **New England Nuclear Corp.** has for commercial use tritiated progestrone, 16-H³ at 1.8 millicuries per mg. Company says this high specific activity greatly extends the detectable range of progestrone in biological systems. C 10

► **National Aluminate Corp.** is marketing three new chemicals the company says appreciably simplify cleaning of boilers and industrial equipment. One, Nalco 85, is alkaline in nature and may be applied to an operating boiler. Nalco clean 66 and 68 are cleaners for industrial process and heat exchange equipment. Both are blends of organic and inorganic acids. C 11

► **Nero-Zinc** is a new green solution to produce deep, lustrous black finishes on plain zinc, die cast, or zinc plated parts in 10 to 120 seconds of immersion time, depending on the temperature of the bath. Wagner Brothers, which formulates the solution, says the product gives finishes with no increase in dimensional tolerance on the treated parts. Possible uses: for camera or instrument parts where nonreflecting surfaces are needed; for identification of small parts where a number of similar ones are handled. C 12

► **A. L. Wilson Chemical Co.** has a liquid preparation, called ExGo, that removes x-ray and photo developed stains from clothes and linens. The company says ExGo may be used on all fabrics and most colors. C 13

► **Circosol NS**, a pale, nonvolatile naphthenic type oil, has been developed by Sun Oil for use as an oil extender in making extremely light-colored butadiene/styrene copolymers. Sun recommends the product where minimum staining and minimum color migration are important to the end use of the finished rubber product. C 14

Further useful information on keyed Chemical items mentioned is readily available...

Use handy coupon on page 86

PLAINTIFF'S EXHIBIT 14

"Industry & Business - Wyandotte to Build",
Chemical and Engineering News, Pages 29, 66
(December 9, 1957)

Pages 777a to 778a

INDUSTRY & BUSINESS

portant to the safety effort is the plant manager. His reason? In any manufacturing enterprise, production is the major risk area.

The plant manager is "Mr. Company" to most employees and to much of the general community, Hannen believes. He is the one who hires and fires, promotes and demotes, "gets along with" (or "fights with") the union. But, he is also the man who gets to the scene of an accident right behind the fire brigade, visits the hospital—and perhaps the widow. His responsibility is to operate a safe plant—and operate at a profit.

Nothing will do more to develop and maintain a supervisor's awareness of the importance of safety than management's demonstrating sincere interest in accident prevention. What can management do to keep accident prevention at maximum effectiveness? R. H. Albisser of Merck says:

- The board of directors can regularly review company-wide safety performance.
- The president can personally review every accident involving serious injury or large loss.
- Top management can let people know that it's sincerely concerned with their safety at all times.

Gibbs Enshrined**Ex-President Hoover lauds Josiah Willard Gibbs and George Westinghouse**

JOSIAH WILLARD GIBBS, generally recognized as one of the great creative geniuses of all time and probably the greatest this country has yet produced, was enshrined on Sunday, December 14, in the Hall of Fame for Great Americans. George Westinghouse was similarly honored. The two bronze busts stand the 85th and 86th to enter the 930-foot open air colonnade on the University Heights campus of New York University.

Gibbs, who was professor of mathematical physics, at Yale, is the second in the Hall of Fame to be recognized for work in chemistry and physics. Joseph Henry, one-time president of the National Academy of Sciences and secretary of the Smithsonian Institu-

tion, was so honored for his work in the same fields in 1915.

Detlev W. Bronk, president of the National Academy of Sciences, commented after the unveiling of the Gibbs bust, that Gibbs' high adventures in the realm of the mind and spirit led to vast practical uses of his physical chemistry throughout modern industry. Early in his career, he became interested in thermodynamics and the relations of heat to other forms of energy. The most creative work of his career, a memoir entitled, "On the Equilibrium of Heterogeneous Substances" was published in 1876 through 1878. But while his greatest work was done in the purest of theoretical science, he never lost his interest in practical problems and his ability to deal with them. An example of the latter is his patent on an improved railroad brake in 1867.

Ex-President Hoover said the accomplishments of George Westinghouse, an engineer, were more familiar to him than those of Gibbs, who taught his specialty for 32 years at Yale. Gibbs was devoted to exploration in pure science and most of his many contributions were made with complete indifference to their application. But, Mr. Hoover added, Gibbs' discoveries in pure science are the raw materials which engineers must transform into useful aids to living for all mankind, and many of his contributions add important comfort to our lives every day.

Westinghouse, said Hoover, was a rare combination of great inventor in the mechanical field, great manufacturer, and great business executive. During his lifetime, he was granted 381 patents, an average of one every month and a half of his working life.

The bronzes of Gibbs were made possible through gifts from Yale University and the AMERICAN CHEMICAL SOCIETY. In addition to the principal fund, contributions came from Ralph C. Van Name, local sections of ACS, Fisher Scientific Co., M. W. Kellogg, the National Academy of Sciences, the American Philosophical Society, AAAS, the American Academy of Arts and Sciences, and others.

The Westinghouse bronzes were provided for by a legacy to the American Society of Mechanical Engineers from Herman Westinghouse, a brother, AIIE, American Society for Engineering Education, Engineers Joint Council, Westinghouse Electric Corp., and Westinghouse Air Brake Co.

Wyandotte to Build

Propylene oxide plant will fill captive needs, leave some for outside sale

PROPYLENE OXIDE CAPACITY in the U. S. will rise early in the second quarter of 1958, when Wyandotte Chemicals plans to bring a new plant on stream at Wyandotte, Mich. It will also make propylene dichloride and dichloroisopropyl ether. Wyandotte has been making the compound on a pilot scale for captive use, has also been buying a good deal of it on the outside. With the new plant, it will be able to fill its needs, sell on the open market too.

This will make Wyandotte the third U. S. firm to offer propylene oxide for sale; Dow and Union Carbide Chemicals are the other two. Celanese Corp. was in the market but withdrew recently. The company says it's still interested on a long range basis, however. Jefferson Chemical plans to make the product at Port Neches, Tex. (C&EN, Nov. 26, 1958, page 5812), with production to start early in 1959. Jefferson will have captive uses, but plans also to sell on the open market.

Foams look fastest. Polyurethane foams look like the fastest moving market for propylene oxide at the moment. Wyandotte's captive uses for the chemical include its Pluronic and Tetronic polyols, which serve both as intermediates for polyurethanes and as surfactants.

In October, Union Carbide announced (C&EN, Oct. 14, page 72) four new polyethers for urethane foams; they are propylene oxide-hexametanol adducts. And Dow has just started volume production of a new family of trihydroxy polypropylene glycols, a special grade of which is being developed for use in urethanes.

Other uses for propylene oxide include making synthetic detergents, propylene and polypropylene glycols, and oil emulsifying and demulsifying agents. Production data for propylene oxide and its derivatives are a bit spotty. However, the Association of American Soap and Glycerine Producers, quoting the U. S. Tariff Commission, gives an average production of roughly 7 million pounds a month of propylene glycol for four of the first nine months of this year. Data were confidential or inconclusive for the other five months.

CHEMICALS



More Aryl Mercaptans Possible

Pitt-Consol develops new process that takes aromatic mercaptans out of specialty class

ANOTHER SPECIALTY PRODUCT GROUP is headed for volume production—the aryl mercaptans: thiophenol, thiocresols, and thioxylenols.

Pitt-Consol Chemicals, subsidiary of Pittsburgh Consolidation Coal, turned the trick with a new process. Still in the pilot plant stage, it is based on extraction from petroleum materials.

In the past, aryl mercaptans were made, in limited volumes, by various synthetic routes. Significance of the new process: substantial price reductions in the final product may cut one half to two thirds off today's price, which goes up to \$2.65 per pound, depending upon the thio chemical concerned.

Pitt-Consol has plans to build a plant to make these chemicals. But company spokesmen point out these plans are geared to market development work now in progress. The results from these studies will determine the time to build a unit. Any facilities added would be at the firm's Newark, N. J., plant. Aryl mercaptan capacity (thiophenol, thiocresols, thioxylenols) might be 3 to 4 million pounds a year.

For comparison, today's estimated output, from synthetic sources, probably does not exceed 700,000 pounds a year. Thiophenol are the biggest taker, somewhere around 500,000 pounds a year. Thiophenol might run 100,000 pounds, while thiocresols are less than that figure.

Hence, Pitt-Consol's new process

will change the production picture sharply. But what about end uses? The company's research and market development staffs are busy exploring possibilities. For example, the —SH group of aryl mercaptans, as compared to the —OH group of phenols, is much more reactive. Lab studies of this —SH activity show it will react in many and varied ways: forms thioethers, S-acylation, chlorinates to make sulfonyl chloride, condenses with acetyl or benzoyl chlorides, and oxidizes to disulfides.

And, quite important, adds the company, is the ability to alkylate the benzene ring—in the past a difficult thing to do. And, when done, yields ran about 50%. Now, Pitt-Consol believes it has a system which gives higher yields—usually over 80%.

Alkylation of the aryl mercaptans has several important effects, adds the company:

- Reduces volatility.
- Moderates odors.
- Improves oil solubility of derivatives.

These properties should allow aromatic mercaptan derivatives to be used in the lubricating oil additive field. Other commercial possibilities include uses as intermediates to make dyes, pesticides, wetting agents, rubber accelerators, organometallic compounds, and pharmaceuticals.

But which areas will hold the most promise is not clear to Pitt-Consol now. But what is quite clear today, adds the company, is that the aryl mercaptans will be out of the specialty class and into the big volume market.

New Polyglycol Group

Dow Chemical has started volume production of a new family of polyglycols. Known as the "11" series, these chemicals are trihydroxy polypropylene glycols based on glycerol. They have three linear chains and three terminal hydroxyl groups.

The series has five members: 11-80, 11-100, 11-200, 11-300, and 11-400. The numer "11" identifies the series, and the second number denotes the viscosity in centistokes at 100° F. Molecular weights of the chemicals range from 700 to 5100. Preliminary tests indicate the new polyglycols have a low order of toxicity, Dow says.

The new polyglycols look promising as nitrocellulose plasticizers and ingredients in hair oil formulations, according to the company. And Dow is developing a special grade for use in urethane polymers.

Polyglycols 11-80 and 11-100 are similar structurally to castor oil, Dow says. Thus they may find use as substitutes for castor oil in many applications. Being synthetic materials, they offer greater stability over castor oil in composition, price, and availability, Dow claims.

▼ ▼ ▼

► **Eastman's rubber antioxidents** are changing their names. Eastozone 30 and Eastozone 31 replace Tenamene 30 and Tenamene 31 for identifying the 2-octyl and 5-methylheptyl derivatives of *p*-phenylenediamine.

► **Spencel** is the name of a new polyurethane series being made by Spencer Kellogg and Sons. The group includes a one-component coating vehicle and a series of two-component systems, one part the prepolymer, the other a catalyst.

► **Cowles Chemical** is now producing diethyltoluamide, a new insect repellent developed by the Army and USDA. Cowles is making the chemical with a minimum meta isomer content of 93%, plans to make an 85% meta product in the future.

PLAINTIFF'S EXHIBIT 15

"Dow Introduces 5 Newcomers in Family of Polyglycols
. . . open new fields of applications", Chemical and
Engineering News, Page 71, (December 16, 1957)

Page 779a

Dow introduces

5 newcomers

in family of polyglycols

Polyglycol 11-80

Polyglycol 11-100

Polyglycol 11-200

Polyglycol 11-300

Polyglycol 11-400

• • • open new fields of applications

How do these members of the new "polyglycol 11 series" differ from their predecessors in the Dow family of polyglycols? They are trihydroxy polypropylene glycols having three linear chains and three terminal OH groups in the molecule.

While the number 11 serves to identify this new series, the second number indicates the viscosity in centistokes at 100°F. The molecular weight ranges from 700 for 11-80 to 5100 for 11-400.

Both Polyglycol 11-80 and 11-100 have similarities to castor oil and, being synthetic materials, offer greater stability in composition, price and availability.

Naturally this new type of polyglycol looks promising in new fields and applications—as a nitrocellulose plasticizer, in hair oils, as a substitute for castor oil in certain applications, and in urethane polymers.

Preliminary investigation indicates Polyglycol 11-80, 11-100, and 11-200 serve as efficient plasticizers for nitrocellulose. Films thus plasticized compare favorably in their main characteristics—clarity, softness, flexibility, and tensile strength—with films using standard commercial plasticizers.

The higher viscosity (and higher molecular weight) members of this series, such as 11-400, show promise in the formulation of hair oils. The similarity of 11-80 and 11-100 to castor oil points to their possible utility in hydraulic fluids.

These new trifunctional polyglycols are available in "Resin Grade" also and have aroused much interest as urethane intermediates. The trihydroxy polyglycol urethane reaction is more readily controlled than the diol reaction and higher hysteresis values on foams can be obtained. Polyglycols 11-200 and 11-300 (Resin Grade)—individually or in combination with other polyglycols—show promise in the manufacture of flexible urethane foams. Foams made with these polyglycols can be formulated to give properties similar to those of foam rubber. Because Polyglycol 11-80 (Resin Grade) is similar to castor oil in structure, it offers possibilities in the production of semi-rigid urethane foams and coatings.

More information or samples of our trihydroxy polypropylene glycols of the new "11 series" are available upon request from Technical Service and Development, THE DOW CHEMICAL COMPANY, Midland, Michigan. Or contact your nearest Dow sales office.

YOU CAN DEPEND ON



PLAINTIFF'S EXHIBIT 16

Letter dated April 7, 1949
From: Charles C. Price
To: G. H. Swart

Page 780a

780a

Pelikan ink 7

University of Notre Dame
Notre Dame, Indiana

10

April 7, 1949

Mr. G. H. Stuart

Director of Research
The General Tire & Rubber Company
Akron, Ohio

Dear Gil:

We have put Ralph Herbst, who has now finished his dissertation research, on the job of making some "propylene Oxide rubber." You remember we discussed this on my last visit to Akron. I am more enthusiastic about the practical application of this than anything I have ever worked on. It should take us only a few months to do the necessary exploratory research. I am therefore writing to ask whether you can appropriate another \$1500.00 to us to cover this work under our existing contract. This will provide for an increase in Herbst's stipend to full time at \$250.00 a month and extra supplies through August, 1949.

Very truly yours,

Charles
Charles C. Price

CCP:fm

PLAINTIFF'S EXHIBIT 17

Letter dated April 18, 1949
From: G. H. Swart
To: Charles C. Price

Page 781a

781a

April 18, 1949

Dr. Charles C. Price, Head
Department of Chemistry
University of Notre Dame
Notre Dame, Indiana

Dear Charlie:

Thank you very much for your recent letter regarding the "Propylene oxide rubber." I am very pleased at your confidence in its practical application. I have talked over the question of financing this particular work and our management is agreeable to appropriating a maximum of \$1500 for this special work. When you next come to Akron we can discuss the problem and the payment more specifically.

I enjoyed seeing you in San Francisco and hope that your trip East to the wedding was enjoyable.

We are hopeful that you will be able to come to Akron in the near future and would appreciate some word regarding your plans.

Yours very truly,

THE GENERAL TIRE & RUBBER CO

G. H. Swart
Director of Research

GHS:mr

PLAINTIFF'S EXHIBIT 18

**Progress Report, re Propylene Oxide-Pentaerythritol
Polymer**

From: Ralph Herbst
To: Dr. C. C. Price
Dated: April 19, 1949

Page 782a

Progress Report

12A

April 19, 1949

To: Dr. C. C. Price

Subject: Propylene Oxide-Pentaerythritol Polymer

From: Charles C. Price and Ralph Herbet

Summary:

Influence of sodium.

A viscous, brown polymer has been prepared by:

(1) a pressure reaction at 140-150° (~85%)

(2) a reaction at room temperature for three days followed by heating at 110-115° (~90%)

In (1) and (2), 6.8 g. (0.05 moles) of pentaerythritol, 70 cc. (1.0 Moles) of propylene oxide-(1,2) and about 1.5 g. of sodium were used. About 0.6 g. of unreacted pentaerythritol was recovered from (1); but none could be obtained from an aliquot portion of (2).

Preliminary studies of the reactions of (1) and (2) with various isocyanates are summarized below:

A- In Absence of Solvent

Polymer	IPD	MDI	OID
(1)	hard, br. polymer	hard, black polymer	waxy solid
(2)	"	" sticky bl. gum excs. MDI	"

B- In Presence of Solvents

(1)	IPD acetone- hard, brown polymer	MDI
	α -chloronaphth- alene- - - rubbery material	diethyl- phthalate-- sticky gum
	diethyl phth- alate- - - "	

IPD- Toluene-2,4-diisocyanate

MDI- Methylene-cis-4-phenylisocyanate

OID- Octadecyl isocyanate

R. Herbet
April 19, 1949

PLAINTIFF'S EXHIBIT 19

**Progress Report, re Propylene Oxide-Pentaerythritol
Polymer**

**From: Charles C. Price and Ralph Herbst
Dated: April 19, 1949**

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Page 783a

121

Received
on 16, 1969

Subject: Propylene Oxide-Pentaerythritol Polymer

From: Charles L. Price and Ralph J. Horne

University of Notre Dame

Summary:

A viscous, brown polymer has been prepared by

(1) a process reaction at 140-150° (N 85%)

(2) a reaction at room temperature for three days followed by heating at 110-115° (N 90%)

In (1) and (2), 6.8 g. (0.05 mole) of pentaerythritol, 70 cc. (1.0 mole) of propylene oxide-(1,2) and about 1.5 g. of sodium were used. About 0.5 g. of unreacted pentaerythritol was recovered from (1); but none could be obtained from an aliquot portion of (2).

Preliminary studies of the reactions of (1) and (2) with various isocyanates are summarized below:

A- In absence of Solvent

Polymer	I/D	N/D	C/D
(1)	hard, brown polymer	hard, black polymer	waxy solid
(2)	"	" sticky bl. gum excs. N/D	"

B- In presence of Solvents

	I/D	N/D
(1)	acetone- hard, brown polymer	
	chloronaphthalene-	diethyl- sticky
	alone- - - rubbery material	Nitrobenzene- black gum
	diethyl ether-	"
	al. 10% " - - -	"
1 -	1, 2, 4, 5-tetraisopropyl	
2 -	ethoxy- <i>c</i> -bis-(<i>c</i> - <i>c</i>) diisocyanate	
3 -	hexamethyl diisocyanate	

783b

Progress Report

April 16, 1949

Subject: Propylene Oxide-Pentaerythritol Polymer
 From: Charles C. Price and Ralph L. Herbst
 University of Notre Dame

Summary:

A viscous, brown polymer has been prepared by

- (1) a pressure reaction at 140-150° (N 85%)
- (2) a reaction at room temperature for three days followed by heating at 110-115° (N 90%)

In (1) and (2), 6.8 g. (0.05 mole) of pentaerythritol, 70 cc. (1.0 mole) of propylene oxide-(1,2) and about 1.5 g. of sodium were used. About 0.5 g. of unreacted pentaerythritol was recovered from (1); but none could be obtained from an aliquot portion of (2).

Preliminary studies of the reactions of (1) and (2) with various isocyanates are summarized below:

A- In Absence of Solvent

Polymer	IPD	MDI	OID
(1)	hard, brown polymer	hard, black polymer	waxy solid
(2)	"	sticky bl. gum excs. MDI	"

B - In presence of Solvents

	IPD	MDI
(1)	acetone- hard, brown polymer	diethyl- sticky phthalate--black gum
	α chloronaphth- alene- -- rubbery material	
	diethyl phth- alate - - -	"

IPD - Toluene-2,4-diisocyanate

MDI - Methylene-bis-4-phenylisocyanate

OID - Octadecyl isocyanate

PLAINTIFF'S EXHIBIT 20

Progress Report, re Propylene Oxide (1,2)-Pentaerythritol
Polymer

From: Ralph Herbst
To: Dr. C. C. Price
Dated May 16, 1949

Pages 784a to 786a

May 16, 1949

~~SEARCHED~~

Subject: Propylene Oxide(1,2)-Pentaerythritol Polymer

From : C. L. Breckin & Ralph H. Lester, Univ. of Illinois

Summary:

Polymers have been made using

- (a) concentrated sulfuric acid as catalyst using a propylene oxide(1,2)-pentaerythritol molar ratio of 20 to 1.
- (b) sodium as catalyst using a propylene oxide(1,2)-pentaerythritol molar ratio of 100 to 1.
- (c) The reaction of (a), (b), and propylene oxide (1,2) polymers, respectively with diisocyanate compounds has been studied.

(a) Sulfuric Acid as Catalyst

With sodium as catalyst, the reaction between propylene oxide(1,2) and aliphatic alcohols has been reported to produce secondary alcohols of the following type: (1)



When acid catalysts such as boron trifluoride and sulfuric acid are used, a mixture of primary and secondary alcohol-ether derivatives are formed. (2) It seemed desirable, therefore, to investigate the polymer produced with sulfuric acid as catalyst. Using propylene oxide(1,2)-pentaerythritol in a molar ratio of 20 to 1 and a small amount of sulfuric acid(conc.) resulted in the formation of a dark brown, sticky gum (y) which was slightly soluble in dioxane, moderately soluble in N-methyl morpholine,

and insoluble in a number of other organic solvents. The reaction between (y) dissolved in N-methyl morpholine and some diisocyanate compounds (3) produced hard, brittle polymers.

(b) Using a Propylene Oxide(1,2)-Pentaerythritol Molar Ratio of 100 to 1 with Sodium as Catalyst

When a molar ratio of 20 to 1 was used, the resulting polymer produced hard, brittle materials upon reaction with diisocyanates (3) - probably due to a large amount of cross-linking. The polymer formed using a ratio of 100 moles of propylene oxide(1,2) to 1 mole of pentaerythritol also produced hard, brittle polymers upon reaction with diisocyanates (3). The same reaction in the presence of diethyl phthalate produced a rubbery material.

(c) The Reaction between Propylene Oxide (1,2) Polymers and Diisocyanate Compounds (3)

Since hard, brittle polymers were still formed using a very large excess of propylene oxide (1,2) as compared to the amount of pentaerythritol used, the reaction between propylene oxide(1,2) polymer and diisocyanate compounds (3) was studied.

About 0.5 g. of sodium was added to 40 cc. of propylene oxide (1,2) and the mixture warmed gently. The reaction mixture after 30 minutes of reaction and the brown solid polymer⁽²⁾ which formed after one day both gave hard, brittle polymers upon treatment with diisocyanates. The same reaction using (z) dissolved in diethyl phthalate produced a hard, rubbery material. All attempts to dissolve this rubbery material in organic solvents have failed.

786a

References:

- (1) & (2) L. A. Petrov(Tashkent Aviation Inst.) J. Gen. Chem. (U.S.S.R.) 14,1039-43(1944); ibid. 16, 1206-12 (1946); O. I. 3081 b (1947)
- (3) Toluene-3,4-diisocyanate, Methylene-bis-*t*-phenyl isocyanate

R. Kehler

PLAINTIFF'S EXHIBIT 21

Progress Report, re Propylene Oxide (1,2)-Pentaerythritol
Polymer
From: C. C. Price and Ralph L. Herbst
Dated: May 16, 1949

Pages 787a to 788a

Progress Report

May 16, 1949

Subject: Propylene Oxide (1,2)-Pentaerythritol Polymer

From : C. C. Price and Ralph L. Forst

University of Notre Dame

Summary:

Polymers have been made using

- (a) concentrated sulfuric acid as catalyst using a propylene oxide (1,2)-pentaerythritol molar ratio of 20 to 1.
- (b) sodium as catalyst using a propylene oxide (1,2)-pentaerythritol molar ratio of 100 to 1.
- (c) The reaction of (a), (b), and propylene oxide (1,2) polymers, respectively with diisocyanate compounds has been studied.

(a) Sulfuric Acid as Catalyst

With sodium as catalyst, the reaction between propylene oxide (1,2) and aliphatic alcohols has been reported to produce secondary alcohols of the following type: (1)



When acid catalysts such as boron trifluoride and sulfuric acid are used, a mixture of primary and secondary alcohol-ether derivatives are formed. (2) It seemed desirable, therefore, to investigate the polymer produced with sulfuric acid as catalyst. Using propylene oxide (1,2)-pentaerythritol in a molar ratio of 20 to 1 and a small amount of sulfuric acid (conc.) resulted in the formation of a dark brown, sticky gum (y) which was slightly soluble in dioxene, moderately soluble in N-methyl morpholine, and insoluble in a number of other organic solvents. The reaction between (y) dissolved in N-methyl morpholine and some diisocyanate compounds (3) produced hard, brittle polymers.

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787

(b) Using a propylene Oxide (1,2)-Pentaerythritol molar Ratio of 100 to 1 with Sodium as Catalyst.

When a molar ratio of 20 to 1 was used, the resulting polymer produced hard, brittle materials upon reaction with diisocyanates (3) - probably due to a large amount of cross-linking. The polymer formed using a ratio of 100 moles of propylene oxide (1,2) to 1 mole of pentaerythritol also produced hard, brittle polymers upon reaction with diisocyanates (3). The same reaction in the presence of diethyl phthalate produced a rubbery material.

(c) The Reaction between Propylene Oxide (1,2) Oligomers and Diisocyanate Compounds (3).

Since hard, brittle polymers were still formed using a very large excess of propylene oxide (1,2) as compared to the amount of pentaerythritol used, the reaction between propylene oxide (1,2) polymer and diisocyanate compounds (3) was studied.

About 0.5 g. of sodium was added to 40 cc. of propylene oxide (1,2) and the mixture warmed gently. The reaction mixture after 20 minutes of reaction and the brown solid polymer (z) which formed after one day both gave hard, brittle polymers upon treatment with diisocyanates. The same reaction using (z) dissolved in diethyl phthalate produced a hard, rubbery material. All attempts to dissolve this rubbery material in organic solvents have failed.

References:

- (1) and (2) A. A. Petrov (Tashkent Aviation Inst.) J. Gen. Chem. (U.S.S.R.) 14, 1023-43 (1944); ibid. 16, 1206-12 (1946); C. A. 3051 b (1947).
- (3) Toluene-2,4-diisocyanate, Methylene-bis-4-phenyl isocyanate.

PLAINTIFF'S EXHIBIT 22

**Progress Report, re Propylene Oxide - Pentaerythritol
Polymer**

From: Ralph L. Herbst
To: Dr. C. C. Price
Dated: August 8, 1949

Pages 789a to 791a

Jeff Davis

789a

AUGUST 8, 1949

To: Mr. [unclear] Progress Report

Subject: - Propylene Oxide/Pentaerythritol Polymer

Summary:-

- (1) A purified P.O.-P.E.T. polymer of molar ratio 200-to-1 was found to have a molecular weight of 640 as determined cryoscopically.
- (2) P.O.-P.E.T. polymers have been "deionized" by passage through Amberlite exchange resins.
- (3) The reaction between P.O.-P.E.T. polymers and anhydride compounds has been studied more quantitatively. Approximately 3-4 parts by weight of P.O.-P.E.T. polymer react with one part by weight of anhydride compound.
- (4) Details of the preparation of P.O.-P.E.T. polymers of molar ratio of 100-to-one and 10-to-1 are given.
*anemic-catalyzed
By-product, gasoline at room temperature, was formed in which case.*

(1) Molecular Weight Determination of 200-to-1 Polymer

The cryoscopic method described by Shriner ("Quantitative Organic Analysis", pg. 64) was employed using redistilled dioxane as solvent. The data are summarized below: (K_w 4.7)

Wt. of sample(g.)	Wt. of solvent(g.)	ΔT	Mol. wt.
0.064	20.660	0.029	655
0.121	"	0.037	626
		Av. <u>640</u>	

Average mol. wt. = 640.

(2) Preparation of "Deionized" P.O.-P.E.T. Polymers

About 1.0 g. of the P.O.-P.E.T. polymer (both 100-to-1 and 10-to-1 were purified in this manner) was dissolved in 30 cc. of redistilled dioxane. This solution was allowed to pass dropwise through a column (1.5 cm. x 8 cm.) packed with Amberlite IR-100-X at atmospheric pressure in about 12 hours. A small portion of the

dioxane solution was shaken with distilled water; the aqueous layer was acidic to litmus. The solution was then passed through the same column containing Amberlite IR-4B in the course of about 8 hours. After shaking a small portion of the dioxane solution with water the aqueous layer was found to be neutral to litmus. The solution was then subjected to vacuum distillation and that portion distilling up to $46^{\circ}/5$ mm. was discarded. The residue was used in the reactions with anhydride compounds.

(3) Reaction between P.O.-P.E.T. Polymers and Anhydride Compounds

Quantitative studies were made of the reaction between P.O.-P.E.T. polymers and anhydride compounds. The amounts of anhydride compounds which gave the best rubbery characteristics are recorded in the following table:

P.O.-P.E.T. Poly.	Anhydride Compd.	Reaction Time	Wt. P.O.-P.E. Wt. Anhyd.
crude 100-to-1 16.4010 g	succinyl chlor. 4.2033 g	125-130°; 24 hrs. 145-150°; 48 "	3.92
100-to-1 ("deion.") 0.6137 g	suc. anhyd. 0.1615 g	125-130°; 12 " 145-150°; 24 "	3.80
crude 10-to-1 2.8300 g	succinyl chlor. 1.0379 g	125-130°; 12 hrs. 145-150°; 24 "	2.72
20-to-1 ("deion.") 4.4253 g	Maleic anhyd. 1.4673 g	125-130°; 12 " 145-150°; 24 "	3.08

Thus about 3-4 parts by weight of P.O.-P.E.T. polymer react with one part by weight of anhydride which is interpreted as meaning there are approximately 4 OH groups per mole of P.O.-P.E.T. polymer, assuming an average molecular weight of about 650.

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(4) Preparation of P.O.-P.E.T. Polymers of Molax Ratio 100-to-1
and 10-to-1.

The quantities of reactants used to prepare these polymers are given below:

P.O.-P.E.T.	sodium (g)	P.O. (cc.)	P.E.T. (g)
10-to-1	2/0	70.0	13.6
100-to-1	0.5	"	1.4

The reactions were carried out in a steel pressure bomb. They progressed as follows:

P.O.-P.E.T. - 10-to-1: Yield, 70%

Time (hrs.)	T, (°C.)	Press. (p.s.i.)
0.0	21	atmos.
0.5	99	110
0.8	135	600
1.0	150	420
1.5	154	410
3.5	152	380
14.	145	320
27.	146	315
30.	145	310
48.	147	310
56.	143	290
one week	room	180

P.O.-P.E.T. - 100-to-1: Yield, 75%

0.0	room	10
0.5	95	50
1.0	120	120
1.3	145	235
1.5 ^x	150	200
3.0	158	180
5.0	160	170
8.0	160	150
10.	163	140
18.	160	110
26.	160	100
33.	160	100
44.	room	40

In both runs gaseous products at room temperature were formed.

Notre Dame, Ind
Aug. 1949

Ralph L. Webster,
Aug. 1949
Charles C. Price

PLAINTIFF'S EXHIBIT 23

Progress Report, re Propylene Oxide - Pentaerythritol
Polymer

From: Ralph L. Herbst and Charles C. Price

Dated: August 8, 1949

Pages 792a to 794a

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792a

Progress Report

Propylene Oxide - Pentaerythritol Polymer

Summary

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Y
- (1) A purified P.O.-P.E.T. polymer of molar ratio 200-to-1 was found to have a molecular weight of 640 as determined cryoscopically.
 - (2) P.O.-P.E.T. polymers have been "deionized" by passage through Amberlite exchange resins.
 - (3) The reaction between P.O.-P.E.T. polymers and anhydride compounds has been studied more quantitatively. Approximately 3-4 parts by weight of P.O.-P.E.T. polymer react with one part by weight of anhydride compound.
 - (4) Details of the preparation of sodium-catalyzed P.O.-P.E.T. polymers of molar ratio of 100-to-1 and 10-to-1 are given. An unidentified by-product, gaseous at room temperature, was found in each case.

(1) Molecular Weight Determination of 200-to-1 Polymer

The cryoscopic method described by Shriner ("Quantitative Organic Analysis", p. 64) was employed using redistilled dioxane as solvent. The data are summarized below: ($K = 4.7$)

<u>Wt. of sample (g.)</u>	<u>Wt. of solvent (g.)</u>	<u>ΔT</u>	<u>Mol. Wt.</u>
0.064	20.660	0.029	655
0.121	"	0.037	626
		Av. 0.033	640

(2) Preparation of "Deionized" P.O.-P.E.T. Polymers

About 1.0 g. of the P.O.-P.E.T. polymer (both 100-to-1 and 10-to-1 were purified in this manner) was dissolved in 30 cc. of redistilled dioxane. This solution was allowed to pass dropwise through a column (1.5 cm. x 6 cm.) packed with Amberlite IR-100-H at atmospheric pressure in about 12 hours. A small portion of the dioxane solution was shaken with distilled water; the aqueous layer was acidic to litmus. The solution was then passed through the same column containing Amberlite IR-4B in the course of about 8 hours. After shaking a small portion of the dioxane solution with water the aqueous

Layer was found to be neutral to litmus. The solution was then subjected to vacuum distillation and that portion distilling up to $45^{\circ}/5$ mm. was discarded. The residue was used in the reactions with anhydride compounds.

(5) Reaction Between P.O.-P.E.T. Polymers and Anhydride Compounds

Quantitative studies were made of the reaction between P.O.-P.E.T. polymers and anhydride compounds. The amounts of anhydride compounds which gave the best rubbery characteristics are recorded in the following table:

P.O.-P.E.T. Poly.	Anhydride Compd.	Reaction Time	Wt. P.O.-P.E.T. Wt. anhyd.
crude 100-to-1 16.4010 g.	succinyl chlor. 4.2033 g.	125-130°; 24 hrs. 145-150°; 48 "	3.92
100-to-1 ("deion.") 0.6137 g.	succinyl anhyd. 0.1615 g.	125-130°; 12 " 145-150°; 24 "	3.80
crude 10-to-1 2.6300 g.	succinyl chlor. 1.0379 g.	125-130°; 12 " 145-150°; 24 "	2.72
10-to-1 ("deion.") 4.4253 g.	maleic anhyd. 1.4673 g.	125-130°; 12 " 145-150°; 24 "	3.03

Thus about 3-4 parts by weight of P.O.-P.E.T. polymer reacted with one part by weight of anhydride which is interpreted as meaning there are approximately 4 OH groups per mole of P.O.-P.E.T. polymer, assuming an average molecular weight of about 650.

Page 3 of Ex 5 stuck here

(4) Preparation of P.O.-P.E.T. Polymers of Volar Ratio 100-to-1 and 10-to-1

The quantities of reactants used to prepare these polymers are given below:

P.O.-P.E.T.	Sodium (g.)	P.O. (cc.)	P.E.T. (g.)
10-to-1	2.0	70.0	13.6
10-to-1	0.5	"	1.4

The reactions were carried out in a steel pressure bomb. They progressed as follows:

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P.O.-P.E.T. 10-to-1: Yield, 70%

<u>Time (hrs.)</u>	<u>T. (°C.)</u>	<u>Press. (p.s.i.)</u>
0.0	21	atmos.
0.5	99	110
0.8	135	600
1.0	150	420
1.5	154	410
3.5	152	380
14.	143	320
27.	145	315
33.	145	310
49.	147	310
56.	143	290
one week	room	120

P.O.-P.E.T. - 100-to-1: Yield, 75%

0.0	room	10
0.5	95	50
1.0	120	120
1.3	145	235
1.5	150	200
3.0	158	180
5.0	160	170
8.0	160	150
10.0	163	140
18.0	160	110
26.	160	100
33.	160	100
44.	room	40

In both runs gaseous products at room temperature were formed.

Ralph L. Herbst, Jr.

Charles C. Price

Notre Dame, Indiana

August, 1949

PLAINTIFF'S EXHIBIT 24

Summary Report, re Propylene Oxide - Pentaerythritol
Polymers

From: University of Notre Dame, Ralph Herbst and
Charles Price
To: General Tire & Rubber Co.
Dated: October 24, 1949

Pages 795a to 798a

23
30.2.

To - Dr. C. C. Price

From - University of Notre Dame

SUMMARY REPORT

Subject Propylene Oxide 1,2,3,4 -Pentaerythritol PolymersObject

To prepare propylene oxide 1,2,3,4 -pentaerythritol polymers and to study their reactions with diisocyanates and anhydride compounds in order to obtain products having rubber-like characteristics.

Summary

Detailed explanations are given of the methods used to prepare propylene oxide 1,2,3,4 -pentaerythritol polymers using sodium and boron trifluoride etherate as catalysts at (a) atmospheric pressure and (b) under pressure- with especial regard for the techniques used and the optimum conditions to be desired. Both catalysts produce propylene oxide 1,2,3,4 -pentaerythritol polymers having molecular weights of about 650. With boron trifluoride etherate as catalyst nearly colorless polymers can be produced while dark brown polymers are produced when sodium is used. In every case one part by weight of an anhydride compound reacted with 2-4 parts by weight of P.O.-P.E.T. polymer.

Reagents

Propylene oxide (1,2) (Eastman Kodak Co.) was redistilled immediately before use; b.p. 35° . Pentaerythritol (Eastman Kodak white label) was used without further purification. Sodium etherate was prepared by passing gaseous boron trifluoride through anhydrous ether at approximately -20° ; m.p. -52 to -50° .

Apparatus

Pressure bomb- For the pressure reactions a 100-ml. cylindrical, stainless steel pressure bomb equipped with a gauge (0 to 800 p.s.i. range) was used. The bomb itself was rated to withstand 10,000 p.s.i.

The glassware and pressure bomb were dried first in an oven at 105 - 110° and then flame dry to insure anhydrous conditions.

Atmospheric Pressure Reactions

For these reactions 140 cc. of propylene oxide was placed in a 300-ml. three-necked flask equipped with a thermometer, mercury-sealed stirrer, and a reflux condenser (60 cm.). At first ground-glass equipment was used but it was found that the propylene oxide dissolved both Lubriseal and Silicone stopcock greases which were used. Tightly-fitting rubber stoppers wrapped in aluminum foil proved satisfactory. Then the appropriate amount of pentaerythritol was added to give the desired molar ratio of P.O. and P.E.T. Low catalyst concentrations were used in order to obtain high molecular weight polymers.

(the type of)

Sodium as Catalyst

The above mixture was cooled to 5° by an ice bath and the sodium added in small portions in the course of about ten minutes. The mixture was allowed to ~~warm~~ to room temperature with vigorous stirring. The mixture gradually became more and more milky and at 18-20° refluxing commenced. The reactions were then heated gradually for various time intervals as summarized below:

P.O.-P.E.T. Molar Ratio	Sodium (g.)	Conditions	Remarks
10 to 1	2.0	25° for 3 days; 110-115° - 1 day	dark brown viscous syrup
100 to 1	1.5	25° for 2 days; 45-50° 1 day	

Boron Trifluoride Etherate as Catalyst

The mixture was cooled to -40° with a Dry Ice-acetone bath and the catalyst cautiously added clockwise with stirring. A violent reaction resulted. Too rapid addition of catalyst caused considerable charring and decomposition. It was found that the reaction could be controlled by adding a drop of catalyst about every two minutes. The reaction mixture was then allowed to rise to room temperature and stirred for a day at the reflux temperature of propylene oxide, 25°. Refluxing was not observed ~~at~~ this temperature. Additional reaction conditions are listed below:

P.O.-P.E.T. Molar Ratio	Bf ₃ .Et ₂ O (cc.)	Conditions	Remarks
50 to 1	0.15	60-85° - 3 days	light tan viscous oils
200 to 1	0.25	60-65° - 2 days; 110-115° - 1 day	

It was necessary to vacuum distil these polymers since a large amount of low-boiling products were produced, (see Research Report August 29, 1949)

Pressure Reactions

The reactants were placed in the steel bomb and the sodium was added in small pieces at room temperature. When boron trifluoride etherate was used as catalyst, the bomb was cooled first to -40° and the catalyst added in the same manner as described for the atmospheric pressure reactions. The bomb was then immersed in an oil bath and heated. Details of the progress of those reactions have been given in previous reports. To obtain an appreciable amount of polymer more than 5 drops of boron trifluoride etherate per 70 cc. of propylene oxide are necessary. When low-boiling products were formed, the pressure rose to a maximum of 380-400 p.s.i. at 165-170°. The pressure did not decrease upon further heating 24 hours longer in this temperature range, however, the pressure decreased to about atmospheric when the reactions were allowed to cool to room temperature. Light tan oils were produced when boron trifluoride etherate was used and dark brown, viscous syrups were formed when sodium was used.

Reactions between P.O.-P.E.T. Polymers and Diisocyanates

Qualitative reactions were carried out between P.O.-P.E.T. polymers and diisocyanate compounds. The procedure used was as follows: About 4-5 cc. of the P.O.-P.E.T. polymer was placed in a test tube and a few drops of the diisocyanate compound added. The toluene-2,4 diisocyanate usually reacted vigorously without heating as evidenced by bubbling and heat evolution. It was sometimes necessary to cool the reaction in running tap water. When methylene-bis-4-phenyl isocyanate was used it was necessary to warm the reaction mixture gently to about 40-50° to start it. Then more of the diisocyanate compound was cautiously added dropwise with stirring until the reaction mixture became viscous. The polymers were cured by additional heating about 10-15 minutes longer. The above-named isocyanate compounds produced hard, brittle polymers while octadecylisocyanate produced viscous oils. A higher temperature was necessary when the reaction was carried out in a solvent; only slight improvement resulted in the "rubbery" properties of the polymers.

Reactions between P.O.-P.E.T. Polymers and Anhydride Compounds

Since hard, brittle polymers were produced with diisocyanates the reactions with anhydride compounds were also studied. The P.O.-P.E.T. polymer was placed in a porcelain evaporating dish and heated on a hot plate to about 125-135°. The anhydride compound was added slowly with stirring in small portions in the course of about two hours. The mixture was then cured by heating for various time intervals usually at 150-160° with continued stirring to prevent a top layer of skin to form until the mixture formed a gelinous mass.

Maleic and succinic anhydrides gave the best rubbery materials. In general the polymers became more hard and brittle the more pentaerythritol present. The results are summarized below:

P.O.-P.E.T. Molar Ratio	Anhydride or Dibasic Acid	Remarks
10 to 1	maleic	black, brittle solid
"	adipic	sticky gum
"	succinic	sticky, rubbery mat.
20 to 1	maleic	tough, hard polymer
200 to 1	succinic	gummy, gelatinous subst.
"	maleic	"
"	succinic	viscous syrup

In every case one part by weight of anhydride reacted with 3-4 parts by weight of P.O.-P.E.T. polymer. This is interpreted as meaning that there are about four hydroxyl groups in the P.O.-P.E.T. polymer since a molecular of about 650 was found cryoscopically.

Additional Remarks

It is to be emphasized that to obtain pure P.O.-P.E.T. polymers it is necessary to remove the alkali from the sodium-catalyzed polymers. This was accomplished by (a) a prolonged operation using HCl gas, (b) passage of polymer through Amberlite resins to produce a "deionized" polymer, and (c) using succinyl chloride instead of an anhydride. For the polymers catalyzed by boron trifluoride etherate it is necessary to remove the low-boiling products by vacuum distillation.

Conclusions

P.O.-P.E.T. polymers having molecular weights of about 650 can be prepared using sodium and boron trifluoride etherate as catalysts. The latter catalyst produced light tan-colored oils while the former produced dark brown, viscous syrups.

The best rubbery polymers are formed by the reaction of these P.O.-P.E.T. polymers with maleic anhydride, succinic anhydride, and succinyl chloride. The reactions with diisocyanates produced hard, brittle polymers.

In future work one should strive to obtain higher molecular weight P.O.-P.E.T. polymers having a greater proportion of high-boiling products.

Notre Dame, Indiana
24 October 1949

Ralph L. Herbold
Charles D. Price

PLAINTIFF'S EXHIBIT 27

**Certified copy of Preliminary Statement of Herbert
L. Heiss, dated September 11, 1959 and
Decision, mailed March 23, 1962 in Interference
No. 90,414**

Pages 799a to 815a

wbw

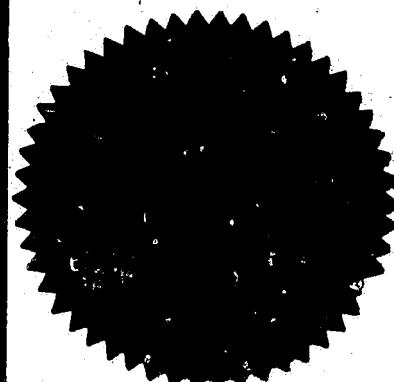
PO-55-Rev
(6-16-61)

799a

U. S. DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE

December 25, 1972
(Date)

THIS IS TO CERTIFY that the annexed is a true copy from the records of this office
of Certain Requested Documents, in Interference Number 90,414.



By authority of the
COMMISSIONER OF PATENTS

W. B. Walder

Certifying Officer.

Mo 218

EXHIBIT OF *Heiss*
1953 A.P.A. 115/57
U.S. Pat. Off., N.Y.

IN THE UNITED STATES PATENT OFFICE

HERBERT L. HEISS }
vs. } INTERFERENCE NO. 90,414
CHARLES C. PRICE }

PRELIMINARY STATEMENT OF HERBERT L. HEISS

COUNTY OF *Dearborn* } SS.
STATE OF *Michigan*

HERBERT L. HEISS, being duly sworn, deposes and says that he is a party to the above-identified interference; that he made the invention set forth by the counts of the interference in the United States:

- (1) THAT no drawing of the invention has been made prior to the filing date of the application Serial No. 373,056, filed August 7, 1953;
- (2) THAT the first written description of the invention was made on November 14, 1951;
- (3) THAT the invention was first disclosed to others on November 14, 1951, and again on March 4, 1952;
- (4) THAT the date of the first act or acts susceptible to proof (other than acts of the character specified in sub-paragraphs 1, 2 and 3 above) which, if proven, would establish conception of the invention was November 14, 1951, these acts consisting of an idea recorded in a laboratory data book and laboratory experiments;

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- (5) THAT the invention was actually reduced to practice on or about January 6, 1955;
- (6) THAT actual exercise of reasonable diligence towards reducing the invention to practice began on or about November 14, 1951.

Herbert I. Heiss
Herbert I. Heiss

Subscribed and sworn before me this 11th day of
September, 1959.

Peter J. Price
Notary Public

My commission expires _____

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Paper No. 78

Final Hearing
November 1, 1961

SL/dlr

IN THE UNITED STATES PATENT OFFICE

BEFORE THE BOARD OF PATENT INTERFERENCES

MAILED

Patent Interference No. 90,414

MAR 23 1962

Price v. Heiss

U. S. Patent Office

Polyether Polyurethane Rubber

Patent granted Charles C. Price December 30, 1958, No. 2,866,774, on application filed September 23, 1953, No. 381,999

Application of Herbert L. Heiss filed August 7, 1953, No. 373,036

Messrs. McCoy, Greene, and TeGrotenhuis for Price

Mr. Elmer P. Rucker, Mr. F. M. Murdock, Mr. Donald J. Haefele, Mr. Clelle W. Upchurch, and Mr. Fulton B. Flick for Heiss

The common invention at issue is concerned with the reaction of an alkylene oxide-polyhydric alcohol condensation product with an organic di-isocyanate.

Counts 1, 3, and 5 are typical of the six counts and follow:

Count 1 A process of forming a polyurethane reaction product comprising the steps of mixing (1) a condensation product of propylene oxide and about .01 to 10 mol percent based on the propylene oxide of an aliphatic polyhydric alcohol of less than 7 carbon atoms and having from 3 to 6 hydroxyl groups, said condensation product having a molecular weight of at least 600 and (2) at least about one mole per mol of condensation product of an organic diisocyanate,

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and reacting the mixture until a second polymer having a chain length substantially greater than that of said condensation product is formed.

Count 3 A process of forming a polyurethane reaction product comprising the steps of mixing in a liquid form (1) a hydroxy terminated polyether glycol polymer having a molecular weight of at least 600 which is a condensation product of an alkylene oxide having from 2 to 4 carbon atoms and about .01 to 10 mol percent based on the alkylene oxide of a polyhydric alcohol having less than 7 carbon atoms and having 3 to 6 primary hydroxyl groups, at least 20 percent of said alkylene oxide having more than 2 carbon atoms, and (2) at least about an equal molar amount of an organic diisocyanate based on said polyether glycol, and reacting the mixture until a second polymer having a chain length substantially greater than that of said polyether glycol polymer is formed.

Count 5 A product made according to process of count 3.

A patent of Price, No. 2,866,774, which issued on an application filed September 23, 1953, is in interference with an application of Heiss filed August 7, 1953. The junior party Price has the burden of establishing priority by a preponderance of the evidence.

The parties filed testimony and briefs and were represented at final hearing.

The interference was apparently declared under the practice set forth in the Commissioner's Notice, 681 OG 865, April 27, 1954. The counts are the involved

Price patent claims with corresponding modified claims of Heiss. Heiss' claims 81 and 82, corresponding to Price's claims 10 and 3, respectively, which are counts 1 and 2, are the only involved claims which omit the "at least 600 molecular weight" recitations of the patent claims. These two claims, with a slight change in claim 82, were suggested to Heiss for interference with the explanation by the Examiner that the counts of the interference would be corresponding patent claims 10 and 3, respectively; see Paragraph 8 of the Office action of March 5, 1959 (paper 19). The four remaining involved Heiss claims contain the molecular weight recitation.

All of the involved Heiss claims also differ from their corresponding Price patent claims in that two of the ranges of patent claims have been changed. The about .01 to 10 mol per cent ratio of the alkylene oxide to the polyhydric alcohol of the patent claims has been changed to 7.5 to 10 mol per cent. As indicated above, it was the Examiner who suggested this narrower range of 7.5 to 10 mol per cent. He evidently adopted Heiss' position that, in Example 12, for instance, the mol percentage was 7.5% - obtained by dividing 13.2 mols of propylene oxide into 1 mol of glycerine and multiplying by 100 ($1/13.2 \times 100 = 7.5\%$). See page 9 of the amendment of February 6, 1959 (paper 18). The Examiner, by going to the top of page 11 of the Heiss application, determined the maximum mol percentage of propylene oxide to glycerine disclosed to be about 33%-($1/3 \times 100 = 33\%$). Therefore, since the Price range of .01 to 10 mol per cent and the

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Heiss range of 7.5 to 33 mol per cent overlapped at 7.5 to 10 mol per cent, he selected this range and suggested it to Heiss.

So too the about an equal molar amount of the condensate to organic di-isocyanate of the patent claims has been changed.

Price contends, pages 9 to 11 of his main brief, that Heiss cannot make the counts for the reasons set forth in his motion to dissolve, which will be discussed below. He also claims a reduction to practice in 1949.

Heiss insists that his application as filed contains a disclosure sufficient to support the counts. He points to the disclosure of the condensate of 13.2 mols of propylene oxide to 1 mol of glycerine of Example XII, among others, which has a calculated molecular weight of about 858 and to the disclosure on page 2 of alkylene oxide condensates of glycerine, tri-ethanolamine and pentaerythritol.

The Examiner, in two decisions (papers 30 and 37), denied Price's motion to dissolve bottomed on Heiss' lack of right to make on the grounds that (1) all of the counts require the at least 600 molecular weight condensates which is a critical limitation, and (2) that the 858 molecular weight of the condensate of 13.2 mols propylene oxide and 1 mol glycerine is an inaccurate assumption. He ruled, inter alia, that the 600 molecular weight was not critical; that because of the overlapping mol ratios of alkylene oxide to polyhydric alcohol "it is reasonable to assume that Heiss inherently obtains a molecular weight

of at least 600"; and that it is immaterial that Heiss fails to disclose a method of making the condensates since both parties filed patents that show them to be old and well known. See page 4, paper 30.

At final hearing, Price again raises the issue of Heiss' right to make, which is ancillary to priority. Podlesak et al. v. McInnerney, 26 App. D.C. 399, 1906 CD 558, 563, 120 O.G. 1222; Smith v. Lane, 43 CCPA 896, 233 F 2d 621, 708 O.G. 516, 110 USPQ 33, 35. Price, therefore, asks us to review the two decisions of the Examiner on this issue.

Since the decision of the Examiner held that the molecular weight recitation of the counts was inherent in Heiss' disclosure, that makes a prima facie case of inherency and the burden is on Price, the junior party, to show lack of inherency; Henning v. Hunt, 42 CCPA 1064, 223 F 2d 926, 106 USPQ 307, 315, 316, which approvingly cited Coast v. Dubbs, 24 CCPA 1023, 88 F 2d 734, 483 O.G. 719, 33 USPQ 91, 96; Pew v. Gard et al., 25 CCPA 1326, 97 F 2d 591, 497 O.G. 553, 38 USPQ 115. To this end, Price has adduced the evidence of a number of witnesses purporting to establish the lack of inherency in the Heiss application.

It is well settled that where an applicant copies a claim from a patent, he must show that he is entitled to make the claim. All limitations in the copied claim will be considered material in determining applicant's right to make the claim, and any doubts arising as to applicant's right to make must be resolved against him. Segall v. Sims et al., 47 CCPA 888, 276 F 2d 661, 753

O.G. 798, 125 USPQ 394, and the citations at 125 USPQ 395.

Heiss' right to make revolves about the recitation in the counts of a "molecular weight of at least 600," a material limitation in the counts. This feature of the counts as such is nowhere disclosed in the Heiss application. But this is not necessarily fatal to the case for Heiss. It is not necessary that each limitation in an interference count must be expressly set forth in haec verba in the disclosure relied upon. It is sufficient if the specification is so worded that the necessary and only reasonable construction to be given the disclosure by one skilled in the art is one that will lend clear support to each positive limitation in the count. Binstead et al. v. Littman et al., 44 CCPA 839, 242 F 2d 766, 718 O.G. 439, 113 USPQ 279, 282.

Turning to the Heiss application, we find that the Examiner, in Paragraph 5 of the Office action of October 2, 1958 (paper 15), rejected, for the first time, then claims 35, 42, 53, 54, and 60, which recited the alkylene oxide-polyhydric alcohol condensates, for lack of disclosure.

There he said that

There is nothing in the specification to indicate how the alkylene oxide-organic trihydroxy compound is prepared, that is, the conditions of reaction (temperature, pressure, catalyst, etc.). Nor is the molecular weight of the condensate set forth.

In response to this rejection, Heiss, on page 11 of the amendment filed February 6, 1959 (paper 18), pointed to his Examples 14, 15, and 17 which disclose

condensates of 13.2 mols propylene oxide and 1 mol glycerine having a molecular weight of about 858 (page 9 of said amendment). To establish his position that these condensates were old in the art at the time of filing his application, Heiss cited patents to Schmidt, No. 1,922,459, and De Groote, Nos. 2,357,933 through 2,357,937.

The Examiner, in view of this showing by Heiss, not only withdrew his rejection, but also, as pointed out above, in his decision on motions (page 4 of paper 30) held that the molecular weight recitation was not critical and the patents cited by both parties show the condensate to be old.

Neither the counts nor the Price specification sets forth the method employed in determining the molecular weight of the condensate. However, Herbst testified that he determined cryoscopically the molecular weight of the 200: 1 propylene oxide pentaerythritol polymer or condensate of Exhibit 5, dated August 8, 1949, to average about 640. (PR, pages 27 to 31). Herbst also testified that assuming a 100 per cent yield of polymer, the 200:1 polymer would be expected to give a molecular weight above 12,000. The witness also testified that the cryoscopic method is usually accurate within about ten per cent, and would be more accurate with polymers having molecular weights from 500 to 1500, but accuracy would be reduced with higher molecular weights (PR. Vol. I, pp. 30, 31, 53, 54).

The experiments of Exhibits 30 and 30 A, summarized in the appendix to the main Price brief, do establish that condensates of 13.2 mols propylene oxide and 1 mol glycer-

ine of molecular weights above and below 600 molecular weight, as cryoscopically determined, may be prepared depending on various conditions. Even Heiss admits this, as witness his evaluation of these Price experiments in which he states, last paragraph of page 17 of his main brief, that:

....Perusal of 30A shows that in the case of condensates of from 13.2 mols of propylene oxide to one of glycerol that the molecular weights determined cryoscopically were in excess of 600, except where water was present...., or where the catalyst was poor or in small amount...., or no catalyst was used....

According to Flores, Heiss' assistant who prepared the polymers of Heiss' Exhibits 4 to 7 in August, 1952, no attempt at that time was made to determine the molecular weights of these polymers, including the polymer of 13.2 mols propylene oxide and 1 mol glycerine of Exhibit 7. This exhibit is dated August 6, 1952. It was not until April 20, 1960 (Exh. I) that the hydroxyl number of the polymer of Exhibit 7 was determined from which a molecular weight of 750 was calculated. Heiss admitted that this was an approximation and not an exact measure of the molecular weight (HR, pages 11, 12).

On the present record, it is an inescapable conclusion that Heiss was in no way concerned with the molecular weight of his condensates until he saw the Price patent and copied certain claims for interference. Even the Schmidt and the De Groote patents relied upon by Heiss to show that the condensates were old in the art, and thus overcome the Examiner's rejection because of lack of disclosure, gave no molecular weights for the condensates thereof. On this record, it appears to have been Heiss' position that, at least at that time (February, 1959), any of the condensates disclosed in his application and prepared according to the processes of the prior art *JTC*

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patents submitted by him would be acceptable to him for the purposes of his invention irrespective of their molecular weights.

Heiss' position before the Examiner was that a condensate of 13.2 mols of propylene oxide with 1 mol of glycerine "has a molecular weight of 857 regardless of how produced." Brief, paper 24, page 4, the sentence beginning in line 5 up. Yet the processes of the experiments of Exhibits 4 to 7, about which Flores testified, were not carried over in the instant Heiss specification. No explanation for this omission has been offered on this record.

Standing alone this omission has no significance. Under the facts of this case, however, it takes on considerable significance and stature because it is urged by Heiss, page 17 of his main brief, that Flores prepared a 13.2:1 condensate of propylene oxide and glycerine "simply upon being told to do so by his superior, Satowski, which is what Heiss used in Examples XI, XII, and XIV to XVII of his application (HR 8)."

There is no question but that, on this record, Heiss' amendment was inspired by the knowledge of what Price had done. It is not enough that he may have had a conception of a process or processes for preparing the questioned condensates (see Flores' testimony regarding the experiments of Exhibits 4 to 7). His application must disclose it; Lindley v. Shepherd, 58 App. D.C. 31, 24 F 2d 606,

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370 O.G. 513. Since Heiss is seeking to rely on this testimony, it would appear that an explanation of why these experiments were not incorporated in the Heiss original application would be in order. Absent such a disclosure, the presumption arising from its omission must be an unfavorable one. Cf. Bowers v. Valley, 32 CCPA 1039, 149 F 2d 284, 579 O.G. 521, 65 USPQ 493, 497.

The quantum of disclosure required to support counts of an interference has been lucidly set forth in Binstead et al. v. Littman et al., supra. There at 113 USPQ 281, 282, the court quoting from Brand v. Thomas, 25 CCPA 1053, 96 F 2d 301, 496 O.G. 561, 37 USPQ 505, 508, stated that:

.....Lack of clear disclosure is not supplied by a speculation as to what one skilled in the art might do or might not do if he followed the teaching of the inventor. The disclosure should be clearer than to suggest that one skilled in the art might construct the device in a particular manner.

Applying the foregoing test to the Heiss original disclosure, we find no clear teaching therein that would point the man skilled in the art to the molecular weight range of the counts, or any molecular weight for that matter.

As pointed out above, the Schmidt and the De Groote patents gave no molecular weights of the condensates thereof. Although his decisions do not expressly so state, the Examiner may or may not have been guided by Heiss' unqualified statement that regardless of how produced such 13.2:1 condensates of propylene oxide to glycerine has a molecular weight of about 857. In any event, the testimony of Herbst and Chase (the experiments

summarized in the Appendix of Price's main brief) and the admission in the Heiss brief, supra, very clearly establish this statement not to be wholly accurate.

We consider that Price has amply discharged the burden devolving upon him to establish lack of inherency in the Heiss original application. The testimony of Herbst and Chase and the admission in the Heiss brief, supra, amply establish that such 13.2:1 condensates may or may not have a molecular weight above about 600. Coupled with a lack of clear disclosure of such a condensate in the Heiss application, we hold that Heiss' disclosure cannot be given the necessary and only reasonable construction by one skilled in the art so as to lend clear support for the positive limitation of the molecular weight range of the counts. Heiss therefore cannot prevail in this proceeding. Binstead et al. v. Littman et al., Lindley v. Shepherd, Segall v. Sims, supra.

The determination of the hydroxyl number of the condensate of Exhibit 7 in April, 1960 (Exh. 1) cannot be accepted to take the place of a test not made in 1952, when the condensate was prepared, and of which Heiss had no knowledge at that time. The law does not recognize nunc protunc tests; Searle v. Glarum et al., 37 CCPA 896, 179 F 2d 974, 635 O.G. 345, 84 USPQ 454, 457; Jira v. Weber et al., 40 CCPA 762, 201 F 2d 914, 670 O.G. 5, 96 USPQ 372, 378; Conner v. Joris, 44 CCPA 772, 241 F 2d 944, 717 O.G. 415, 113 USPQ 56, 61.

According to Sherwood's testimony (HR, pages 75 to 78), the analysis of Heiss' Exhibit 1 was performed by one John

Bombe, who was not called to testify. Therefore, this data sheet of itself, not having been properly proved as to the accuracy of their contents, can not be held to be evidence of such contents; Teter v. Kearby, 36 CCPA 706, 169 F 2d 808, 617 O.G. 903, 79 USPQ 65, 72; Farrington et al. v. Mikeska, 33 CCPA 1073, 155 F 2d 412, 509 O.G. 3, 69 USPQ 509, 511.

To accept Kosmin's testimony that the specific process he used would, in 1953, produce a 13.2:1 condensate of propylene oxide and glycerine of a molecular weight of at least about 600, would practically negate the effect of refusing to accept Flores testimony as a conception because it was not disclosed. Lindley v. Shepherd, *supra*. Similarly, Kosmin's specific process is not disclosed.

The quote from Brand v. Thomas, extracted in the Littman et al. case, *supra*, makes it abundantly clear that the disclosure should be clearer than to suggest that one skilled in the art might produce the condensate in a particular manner. Consequently, since Kosmin's particular process can not be bottomed on the Heiss application, it carries little probative value. Cf. In re Smyth, 38 CCPA 1130, 189 F 2d 982, 651 O.G. 5, 90 USPQ 106, 112, where affidavits to explain a disclosure were not considered.

We turn now to the omission of the molecular weight limitation in Heiss claims 82 and 81, which are stated by the Examiner to be modified claims corresponding to Price's claims 3 and 10, respectively, which are counts 1 and 2, respectively. We do not regard the molecular weight limitations of these two counts to be immaterial ones whereby they may be omitted under the practice

set forth in Parker v. Craft et al., 1919 CD 72, 265 O.G. 305; Bonine v. Bliss, 1919 CD 75, 265 O.G. 306. Throughout the ex parte prosecution of the Price application, heavy reliance was placed on the molecular weight limitations, which appeared in all of the claims except claim 17, which, as explained, inadvertently recited at least about 500, to carry the claims over the cited art. This alone establishes the molecular weight recitations to be an essential and material limitation.

Contrary to Heiss' arguments, the Price specification does establish the molecular weight limitation of the counts to be an essential and material limitation, as witness Column 1, line 53 to Column 2, line 6, and Column 2, lines 14 to 53. We are not persuaded that the Examiner, in view of such disclosure, properly took the position that the limitation was an immaterial one.

The test is whether the counts of the interference and Heiss' modified claims are for the same invention; McCabe v. Cramblet, 20 CCPA 1220, 65 F 2d 459, 437 O.G. 576, 18 USPQ 71. There is a decided difference in scope between these two sets of claims. Heiss' claims 82 and 81 are broader than the corresponding counts. It has been held that the fact that a broad claim embraces the subject matter of a narrower one does not, in itself, establish that the two are drawn to the same invention; Andrews v. Wickenden, 39 CCPA 860, 194 F 2d 729, 659 O.G. 305, 93 USPQ 27; Emerson v. Beach, 42 CCPA 711, 215 F 2d 290, 691 O.G. 170, 103 USPQ 45.

In the light of these two cases, we are constrained to hold that Price claims 3 and 10 and Heiss claims 82 and 81 minus the molecular weight limitations, are not for the same invention.

In the light of the foregoing discussion, we conclude that the Examiner improperly considered the molecular weight limitations of Price claims 3 and 10 to be non-essential and immaterial limitations. Heiss, therefore, cannot prevail here on counts 1 and 2; the Parker, McCabe, Andrews and Emerson cases, *supra*.

In short, Heiss has no clear basis in his application as filed for the limitation in question. He, therefore, cannot prevail in this proceeding.

Having reached the conclusion that Heiss cannot make the counts other issues presented by the parties need not be considered. *McBerty v. Shore et al.*, 1912 CD 45, 49, 175 OG 843; *Eger v. Watson*, 26 CCPA 1411, 104 F 2d 953, 509 OG 779, 42 USPQ 157, 161; *Giambalvo v. Detrick et al.* 35 CCPA 1112, 168 F 2d 116, 77 USPQ 582, 586.

Priority of invention of the subject matter in issue is hereby awarded to Charles C. Price, the junior party.

J. Isaacs
J. Isaacs
Examiner of Interferences

Warren H. Willner
Warren H. Willner
Examiner of Interferences

S. Levin
S. Levin
Examiner of Interferences

BOARD
OF PATENT
INTERFERENCES

PLAINTIFF'S EXHIBIT 28

Memorandum dated June 21, 1954
From: Elmer P. Rucker
To: J. H. Saunders

Page 816a

FROM MONEL METAL COMPANY

816a

Herbert L. Meiss

A: St. Louis, Missouri

D.D. June 21, 1954

To: J. H. Saunders Reference

At: Anniston, Alabama Subject: Saunders et al. application
Serial No. 373,036 Filed
August 7, 1953
NOVEL RESINOUS COMPOSITIONS
AND METHOD OF PRODUCING SAME

I am enclosing herewith a copy of the above entitled application together with the initial office action and the references cited therein.

Will you kindly go over this action and the references carefully and advise me wherein the invention claimed is distinguishable from the disclosures of these references. It would appear from a superficial examination of the references that the broad reaction of polyisocyanates with urethanes is anticipated..

I would appreciate receiving your comments at least by the end of this month if possible.

Elmer P. Rucker

Elmer P. Rucker

EPRja Elmer

I have to agree with the Examiner that our broad claims aren't valid. I believe we do have two novel points - making foams from urethanes + isocyanates (with a strong catalyst), & gelling the compatible organic liquids (e.g. Acetone). Would it be appropriate to refile, covering these separately & specifically? If so, delete my name from the application on gelling the liquids.

Jim

PLAINTIFF'S EXHIBIT 29

Short Form Report No. 2914: "The Preparation of Potting Resins from Diisocyanates, Triols and Plasticizers"

Work Started: June 1952
Work Completed: March 1953
Date Reported: September 30, 1953
From: J. H. Saunders

Pages 817a to 819a

This report and the information contained herein is the property of
MONSANTO CHEMICAL COMPANY

HEISS DEPO

EX. #28 (id)

11-16-71 MS

RESEARCH DEPARTMENT - PHOSPHATE DIVISION

SHORT FORM REPORT

Report No. 2914

Distribution: Messrs:

Work Started: June 1952

Research File

Work Completed: March 1953

R. L. Jenkins - St. Louis

Date Reported: September 30, 1953

M. V. Moss - St. Louis

Job No.: 750.01-1080

C. A. Hochwalt - St. Louis

File No.: 451-C-1

N. N. T. Samaras - Dayton

Investigators: J. H. Saunders

E. E. Hardy

H. L. Heiss

J. R. Wilson - St. Louis

B. R. Davis

C. H. Hall - St. Louis

H. F. Weaver - St. Louis

J. H. Saunders

H. L. Heiss

Extra (2)

This Copy For Extra (2)

TITLE: The Preparation of Potting Resins from Diisocyanates, Triols and Plasticizers.

INTRODUCTION: During the course of other work it was observed that liquid plasticizers such as Aroclor 1242 could be gelled with diisocyanate-polyol reaction products. Because such materials have a potential use as potting resins the gelling of plasticizers was explored briefly.

SUMMARY: A number of Aroclors and other plasticizers were solidified with the reaction products of diisocyanates and triols. A 2:1 ratio of isocyanate to hydroxyl groups was used, and the reaction product of the isocyanate and triol, dissolved in the plasticizer, was cured at elevated temperatures. Reaction of isocyanate groups with urethan groups presumably provided the curing.

Although some clear, bubble-free resins were obtained, no method was found whereby consistently good resins could be prepared.

CONCLUSIONS: The gelling of plasticizers by diisocyanate-polyol adducts containing free isocyanate groups is accompanied by gas evolution during the curing of the adduct. Other methods of curing, such as the reaction of the adduct with more polyol or polyamines should prove more successful. The reaction of polyisocyanates and polyols at a 1:1 ratio of isocyanate to hydroxyl groups might also give better results.

RECOMMENDATIONS: It is recommended that further work on preparing potting resins follow the lines indicated in the conclusions.

J. H. Saunders
J. H. Saunders

PREVIOUS WORK: No work has been done previously on this problem.

EXPERIMENTAL DATA: Note book pages: 89901 - 89907, 89910 - 89916,
 89918 - 89950, 85101 - 85103,
 85105 - 85107, 78960 - 78969,
 78971 - 78978, 78981 - 78983,
 78989 - 78994, 78997 - 79000.

Experiments were performed by dissolving the triol in the plasticizer and adding the diisocyanate, with stirring. When the triol was triethanolamine or an ethylene oxide condensation product of triethanolamine a solid product separated after the isocyanate was added. The liquid portion of the reaction product was gelled by heating for 6 hr. at 150°C.

When ethylene oxide and propylene oxide derivatives of glycerine were used no solid by-product was formed in the first step of the reaction. When diols were used instead of triols no gellation of the plasticizer occurred.

Preliminary reactions using plant grade TDI were violent and uncontrollable. Use of TDI deactivated with a trace of dry HCl permitted controlled reactions and gave liquid solutions which could be converted to solid resinous material by heating.

The plasticizers indicated below were gelled when equal weights of plasticizer and isocyanate-triol adduct were used. The triol used was the condensate of glycerine with 13.2 moles of propylene oxide. Plasticizers which were compatible with the adduct, all of which were gelled, were Aroclors 1148, 1221, 1232, 1248, 1254, 1260, 1268, 4465, 5442, 5460, HB-40, chlorinated trimethylphenylindane (IN-420), chlorinated naphthalenes, Paraplex G-60 (polyester), tricresyl phosphate, Santicizer 141 (2-ethylhexyl diphenyl phosphate), Santicizer B-16 (butyl phthalyl butyl glycolate), styrene, and dimethoxy tetraethylene glycol. Di-2-ethylhexyl phosphite was compatible, but was not gelled. Thiokol ZL-109, a polyisobutylene plasticizer, dodecylbenzene and a silicone oil were not compatible.

MDI (diphenylmethane diisocyanate) was substituted for TDI in gelling Aroclor 1242 with similar results. Plant grade MDI-100 gave uncontrollable reactions, but after adding a trace of dry HCl to the MDI normal reactions were obtained.

In one series of experiments using Aroclor 1242, TDI and glycerine plus 13.2 moles of propylene oxide the Aroclor content was varied, using 20, 35, 65 and 80% Aroclor. Those resins with 65 and 80% Aroclor were softer than those with 20 and 35% Aroclor, and required longer heating to bring about gellation.

Most of the cured resins contained bubbles of trapped gas. This was especially noticeable when TDI or MDI which had not been acidified with HCl were used. Bubble-free resins up to approximately 0.25 in. thick could be prepared, but thicker resins almost invariably contained bubbles.

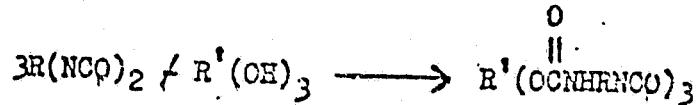
Careful drying of the triols over calcium hydride failed to eliminate bubbling.

Temperature characteristics of a number of resins were investigated briefly. Several series were tested, some in which the Aroclor 1242 content was varied and some in which other Aroclors and plasticizers were used. All of the resins were altered physically at temperatures of about 300°C. All tended to bleed Aroclor or other plasticizer at this temperature. At temperatures of about 200°C the resins were altered only slightly or apparently none at all.

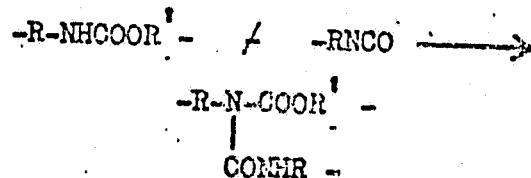
None of the resins containing Aroclor which were tested would support combustion with the exception of one which consisted of 50% Aroclor 1242 and 50% of the adduct of TDI and a 12 mole ethylene oxide-condensate of glycerine. The same resin with higher Aroclor content (65%) or higher molecular weight Aroclor would not support combustion.

Resins prepared using the Aroclors had dielectric constants of 4 - 5 and power factors of 2 - 5%.

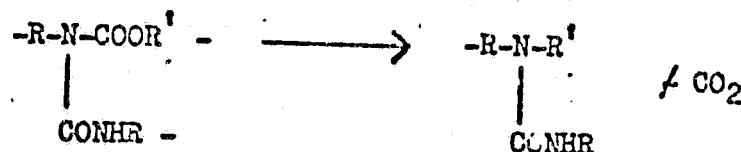
DISCUSSION: The isocyanate-triol adducts were assumed to have the following structure:



In the absence of other active hydrogen compounds these adducts could cure further by reaction with the urethan groups:



The gas evolution could have come from the N-carbamyl-carbamate groups:



Gas evolution has been noted in the formation of acylcarbamates, closely related materials (Ben-Ishai and Katchalski, J. Org. Chem. 16, 1025 (1951)).

PLAINTIFF'S EXHIBIT 33

Letter dated August 11, 1965
From: C. W. Upchurch
To: Farbenfabriken Bayer

Pages 820a to 821a

MOBAY CHEMICAL COMPANY

PENN LINCOLN PARKWAY WEST • PITTSBURGH 5 PENNSYLVANIA

August 11, 1965

Farbenfabriken Bayer, A.G.
 Patentabteilung
 Leverkusen-Bayerwerk
 West Germany.

Gentlemen:

In order that you will be kept advised of Mobay's licensing plans, I would like to describe briefly three license programs we are now considering.

As you know, we were granted the Heiss patent 3,102,875 after the Price patent interference had been concluded. In our opinion, this patent dominates the Price patent and we believe that it is being infringed by everyone making polyether based polyurethane foams. We have attempted to license the patent to polyol producers following a plan similar to that used by General Tire in licensing its Price patent. However, we have experienced considerable difficulty because the polyol producers reply that the patent is used by Mobay's customer as well as the polyol customer so immunity from suit should be issued by Mobay.

In an effort to place the patent in a position where it can be exploited, we are negotiating with Jefferson Chemical Company. The patent will be assigned to Jefferson and Jefferson will attempt to license its polyol competitors. The argument the polyol producers have been using will no longer be applicable.

Jefferson's interest in the proposal was not very great until we offered to include some other patents which would be of interest to them. We have two Ertman patents 2,949,431 and 3,036,020 directed to the preparation of foams using particular tertiary amine catalysts. Mobay does not want to be in the catalyst business. Jefferson plans to use these patents in connection with its production of catalyst.

Our Mo. 253 application as you know, is directed to the preparation of foams using oxyalkylene block copolymer stabilizers. Our Mo. 266 application, assigned jointly to Bayer and Mobay, is directed to the use of the same stabilizer but in conjunction with Dabco. Jefferson prefers the first of these two applications and we will probably include an assignment of it in the agreement. The reason for including the application is to provide Jefferson with some leverage in negotiating with Carbide who makes the stabilizer.

The Heiss patent 3,143,517 which also was granted on the application which became 3,102,875, has three claims in it directed to the preparation of polyurethanes with N-alkyl morpholine catalyst. We propose to assign the patent to Jefferson because they compete with Carbide in making N-alkyl morpholine and believe that they can license this patent to Carbide and use it in their negotiations with respect to the Heiss patent.

The proposed arrangement with Jefferson hinges on whether or not Monsanto will assign its half of the Heiss patent to Mobay. I understand that Monsanto has agreed to this but the question of whether or not Mobay should pay Monsanto has not been resolved. There does not appear to be any problem with respect to Daylor patents because in all probability, Mo 253 will be used instead of Mo 266.

The proposed agreement with Jefferson provides Mobay with a minimum of \$50,000 from Jefferson. If Jefferson cannot license another polyol producer within two years, Jefferson is to pay Mobay a total of \$90,000 and will reassign Mo 253 and U.S. 3,102,875 to Mobay. If Jefferson is successful in licensing competitors, the royalties collected will be split on a 60-40 basis with Mobay. Mobay will net from \$410,000 to \$450,000 after taxes, if Jefferson signs all the other polyol producers depending upon the time required for Jefferson to grant the license.

We have proposed an agreement with M and T under our Mo 277 application which covers the use of stannous salts in making foam. M and T is agreeable to paying us \$.05 per pound on all catalyst sold in any country of the world where we have a patent. The agreement includes a minimum of \$50,000 to be paid in \$12,500 installments over a period of three years as a minimum advance payment of royalties to become due under the agreement. We have selected this as preferable to the assignment of our Japanese patent to Yoshitomi for \$100,000. We have a license with Yoshitomi before MITI for approval now which guarantees us a minimum of \$35,000. We believe that we will make more money with the M and T license plus the Yoshitomi license than we would make by assigning the Japanese patent to Yoshitomi. M and T would not be interested in our foreign rights without Japan being included.

PLAINTIFF'S EXHIBIT 34

Letter dated July 29, 1965
From: C. W. Upchurch
To: B. R. Nason

Pages 822a to 824a

822a
July 29, 1965

Mr. B. R. Nason
Pittsburgh

Proposed License Agreements

11-8-71

EP

The Monsanto/Bayer contract does not require Mobay to obtain approval of the licensing of use patents but it has been the practice in the past to bring these matters before the Board, particularly where a major license is concerned. I believe you might want to advise the Board of Mobay's intentions with respect to the following proposed agreements.

1. Mobay/Jefferson Chemical Agreement:

Mobay has not had much success in licensing polyol producers under Heiss Patent No. 3,102,875. This patent is owned jointly by Mobay and Monsanto and dominates the Price patent. It covers the preparation of a polyurethane while using polyethers having 3 or 4 hydroxyl groups.

It is believed that Jefferson can be more successful in licensing polyol producers. Jefferson can enforce its patent against customers of other polyol producers. Mobay has not been in this position because most of the polyol producers' customers are to some extent Mobay customers, too.

We propose to assign Heiss Patent 3,102,875 to Jefferson. In attempting to license the patent, we propose to leverage for Jefferson to use in attempting to license the patent, we propose to assign U.S. Patents No. 2,949,431 and 3,036,020 which are of no commercial value to Mobay because they are directed to the preparation of foams using a particular tertiary amine catalyst. Jefferson manufactures tertiary amines and believes these patents will be helpful in some of the negotiations with other producers.

We propose to assign U.S. No. 3,143,517. This patent is also owned jointly by Mobay and Monsanto. Three of the claims of the patent are directed to the preparation of foams with an N-alkyl morpholine catalyst. Jefferson makes such catalysts. This patent should help in negotiations to license Heiss 3,102,875.

Mobay will assign a patent application directed to a one-shot process for making foam using an X-520 type silicone and a tertiary amine catalyst. This application is considered important by Jefferson because of proposed negotiations with a competitor.

In each instance where Mobay assigns a patent, it will receive a non-exclusive license for Mobay, Bayer and Monsanto with one exception that with Hcius 3,143,517 Mobay and Monsanto will receive an exclusive license under all the claims except the three directed to the use of the N-alkyl morpholine. The latter three claims will be licensed non-exclusively to Mobay and Monsanto.

In return for the foregoing assignments, Jefferson will pay Mobay a minimum of \$50,000 and attempt to license other polyol producers. The minimum royalty under the license to others will be \$200,000 each. Mobay and Jefferson will split these license fees on the basis of 60% to Jefferson and 40% to Mobay. Jefferson has two years in which to grant at least one license to a major polyol producer. If it has not licensed one by the end of the first year of the agreement, it will pay \$10,000 quarterly to Mobay until the end of the second year or until one major competitor has been licensed. The result is that if Jefferson is unsuccessful in two years, Mobay will receive \$90,000 and the Heiss Patent and the patent application described above will be re-assigned to Mobay. If Jefferson is successful in licensing all the other polyol suppliers, Mobay will receive \$410,000 to \$450,000, after taxes, depending upon the time the first licensee signs. Jefferson would net \$310,000 after taxes.

Mobay will grant Jefferson the right to extend immunity from suit for infringement of the claims of the basic polycether patent, Windemuth 2,949,691 to customers while using Jefferson's polyol in making caulk and sealants. We have previously granted royalty free licenses under the patent to some manufacturers of caulk and sealants. In return for the license to Jefferson, we will receive a license under three U.S. patents in the isocyanate field which might prove of interest later.

2. M and T License:

Mobay has licensed Yoshitomi non-exclusively under any patent we obtain in Japan, covering the use of a stannous salt catalyst in making foams. Yoshitomi is to pay a 5% royalty based on the selling price of the catalyst with a minimum of \$35,000. As an alternate, Yoshitomi has stated it would pay Mobay \$100,000 for an assignment of this Japanese patent.

M and T has offered to pay Mobay \$.05 a pound on all catalyst it sells in any country of the world where Mobay has a patent. At the present time, we have patents only in countries where there is no opposition procedure. However, we have filed opposition in Australia and expect to win the opposition in other countries. We have won the interference with General Tire in the United States. We hope to issue this patent within the next year.

Under the proposed M and T agreement, Mobay will receive \$12,500 as an advance payment of royalties when the Japanese patent issues. It will receive additional payments of \$12,500 on the first and second anniversaries of the agreement. A fourth payment of \$12,500 to be made on the third anniversary date of the agreement or when the U.S. Patent issues, whichever is later. These four payments of \$12,500 each represent a \$50,000 minimum royalty from M and T. In addition to this minimum, M and T will pay \$.05 a pound royalty on all catalyst it has sold since the issue date of the patents we presently have. A rough calculation estimates this would come to \$5,000 - \$10,000.

M and T has indicated that it is presently selling from 500,000 to 600,000 pounds catalyst per year in those countries where we expect to obtain a patent. It appears that Mobay would stand to make more money if it accepts the M and T proposal and retains its Yoshitomi license, so we propose to license M and T at \$.05 a pound and attempt to obtain approval of the present Yoshitomi license by MITI.

Original signed by C. W. Upchurch

PLAINTIFF'S EXHIBIT 37

Memorandum dated September 6, 1957
From: J. H. Saunders
To: C. W. Upchurch

Page 825a

825a

From MOBAY CHEMICAL COMPANY

cc H. Kittner

At New Martinsville

Date September 6, 1957.

To C. W. Upchurch

Reference CWU/FILE, 8-22-57

At St. Louis

Subject PREPOLYMER 4910

SEP 9 1957

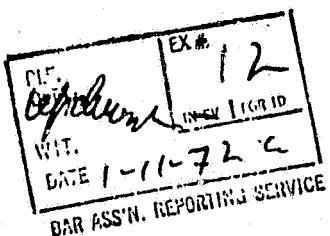
PATENT DEPARTMENT

Development file

Your reference memo indicates that I did not describe prepolymer 4910 clearly enough. This prepolymer is prepared from 60 parts of polypropylene ether glycol 2025 and 40 parts of a triol having a molecular weight of 3000. The triol is prepared by condensing glycerin with propylene oxide to the desired molecular weight. Such a product is represented by Dow Triol 11-200 and by Carbide "NIAX" Triol LG-56.

J. H. Saunders

JHS:mj



PLAINTIFF'S EXHIBIT 38

Memorandum dated January 2, 1962
From: Cleelle W. Upchurch
To J. R. Wilson

Page 826a

Pittsburgh

826a

I. F. M. Murdock
Mr. R. L. Sternberg
Mr. J. D. Upham

January 2, 1962

Mr. J. R. Wilson

Monsanto - St. Louis

MONSANTO BRITISH SPECIFICATION
No. 793,780 - APPLICATION No. 22,904/54

The above British application corresponds to the one involved in the Price patent interference in this country. The application was published before the Price patent issued and does not have claims directed to the invention covered by the Price patent. I have been told by MCL's attorney that we cannot now add such claims.

The invention covered by the published claims and by those now being presented involves adding a plasticizer to a reaction mixture containing a polyisocyanate and a polyhydroxy compound. The inventor found that a polyurethane can best be plasticized if the plasticizer is present as the polyurethane is formed.

The invention is not used in this country commercially at this time. It is of such a nature, however, that there is a possibility it will find some use as the elastomer field expands.

Your proposed method of handling the opposition and any patent which issues appears to be a good one.

Incidentally, a more important application in Great Britain is Monsanto's basic polyether-polyurethane application. I do not have a copy of the file of this application, but understand that it was published as Specification No. 769,091 (Monsanto 1952). This application is apparently being opposed by DuPont. The disclosure will support claims which cover the invention claimed by Price in his U. S. patent. I should think that you would be in a good position to sell a license to ICI under any patent resulting from this application.

Original signed by C. W. Upchurch

Cleelle W. Upchurch

PLAINTIFF'S EXHIBIT 39

Letter dated March 31, 1964
From: Clelle W. Upchurch
To: Farbenfabriken Bayer

Page 827a

827a

March 31, 1964

Farbenfabriken Bayer AG
Leverkusen-Bayerwerk
West Germany

Attention: Patentabteilung

Gentlemen:

British Patent No. 793,780

I am enclosing a copy of British Patent 793,780. This patent issued on the application corresponding to the one in the Heiss-Price interference in this country. We were unable to obtain claims in Great Britain corresponding to the ones in our U. S. 3,102,875 because claims of the type in the British patent had already been published when we learned of the Price patent.

Very truly yours,

Original signed by C. W. Upchurch

Clellie W. Upchurch
Director of Patents

CWU/iml

Enclosure

PLAINTIFF'S EXHIBIT 40

Letter dated September 13, 1963
From: C. W. Upchurch
To: J. H. Sutherland

Page 828a

828a

September 13, 1963

Mr. J. H. Sutherland
Suite 1004, Shell Building
1221 Locust Street
St. Louis 3, Missouri

Dear Jack:

U. S. Patent 3,102,875 - MO-213-U

Mr. Mahoney has asked for an opinion on the "strength" of the subject patent. I am enclosing a copy of the patent and a copy of the file in the Patent Office. Under separate cover I am sending the interference proceedings; these are our file copies, which should be returned to us after you have formulated your opinion.

I would like to have your opinion as to whether or not this patent could be successfully enforced against an infringer. You should note particularly that we did not start specifically claiming a process for making a polyurethane from a polyether having more than two hydroxyl groups until the amendment was filed in January 1958. Up to that time, the claims had included limitations which required the use of a plasticizer or foaming in the presence of alkaline catalysts.

The file includes the prior art cited by the Examiner. I am not aware of any prior art which is any more pertinent than the Windemuth et al. Patent, U. S. 2,948,691; however, there is a Hill Patent, U. S. 2,929,300, which can claim a filing date of July 19, 1951, insofar as the use of polyethers having two hydroxyl groups is concerned. I am enclosing a copy of this patent. There was also some work in this field by ICI. I am enclosing a copy of Canadian Patent 563,470. You will note that this patent discloses linear polyurethanes.

This question will probably be discussed at a Board Meeting about the middle of October, so I will appreciate it if you will furnish me with your opinion prior to that time.

Very truly yours,

CWU/ihm
Enclosures

Original signed by C. W. Church

PLAINTIFF'S EXHIBIT 41

Memorandum dated March 15, 1965
From: Carl G. Ries
To: File

Page 829a

J. FERSON CHEMICAL COMPANY, INC.

FILE MEMORANDUM

DATE 3-15-65

SUBJECT: Mobay -- Meeting with
Messrs. Mahoney and Upchurch

COPY TO:

On Tuesday, March 9, 1965, at 11:00 o'clock a.m., Dr. Sommer, Dr. McCleary, Messrs. Griswold, Dowding and Ries met with Mr. Mahoney, President of Mobay, and Mr. Upchurch, Patent Counsel, for the purpose of discussing a proposed licensing arrangement with Mobay pursuant to which Jefferson would acquire certain licenses under certain of their patents and a patent application. Mr. Upchurch was of the opinion that all of the patents were good and that their asking price of \$200,000 was quite reasonable, since we would "get it back" without any trouble.

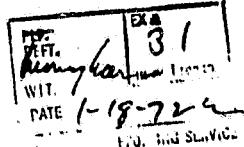
I pointed out that many of the patents are directed to products that are not now being manufactured and sold on a commercial scale and that, therefore, any remuneration that might be derived from these patents was problematical. As to the first Heiss patent, I indicated that there is doubt as to its validity and to the propriety of approaching Jefferson rather than the foam manufacturers.

As to the second Heiss patent, I indicated that I feel the Orth patent owned by Minnesota Mining and Manufacturing Company is a very close reference which casts a cloud of doubt on its validity.

After discussing the foregoing points, it was concluded that we could not come to an understanding at the present time, and further study was required.

Dr. Sommer then told Mr. Mahoney that we would make a counteroffer in writing within the next two weeks, and Dr. Sommer and Mr. Mahoney agreed that they would get together in Pittsburgh on April 15 to discuss the subject further.

Carl G. Ries
Carl G. Ries 115137



CGR:rb

PLAINTIFF'S EXHIBIT 60

Memorandum dated February 13, 1953
From: H. Heiss
To: E. P. Rucker

Pages 830a to 831a

830a

MONSANTO CHEMICAL COMPANY

At Anniston, Alabama

cc L. Jenkins - St. Louis
E. Hardy
T. H. Cleveland
J. H. Saunders
Research File - Anniston

Date February 13, 1953

To E. P. Rucker

Reference

At Anniston

Subject SOLIDIFICATION OF FLUIDS WITH ISOCYANATES

It has been demonstrated that fluids may be solidified by polymerization of diisocyanate-polyol adducts dissolved therein. The resulting solid may vary from a soft gel to a hard brittle resin (depending on the types and amounts of constituents used) and apparently consists of a complex polyurea-urethane plasticized by that fluid. Depending on the type of product desired, the di-isocyanates and polyols (or other active hydrogen compounds) are reacted as described in H. L. Heiss patent application Serial No. 300,968, reaction taking place in the fluid which it is desired to solidify. The resulting mixture is usually a viscous liquid which is stable for a considerable length of time if stored at room temperature in tightly closed containers. When this mixture is heated (for example about 5 hours @ 150°C.) it is transformed into a solid material. Water or other active hydrogen compounds are not required for this solidification, since the free-NCO groups of the dissolved adduct evidently react with the urethane groups also present to form a highly cross-linked polymer. If, however, active hydrogen compounds are present, they will also enter into the reaction. For instance, when the liquid mixture is solidified in an open container, the surface exposed to the air will usually cure to a tougher type of material than will the bulk of the liquid. It is believed that this is due to reaction of atmospheric moisture with the adduct.

The notebook pages to which we refer will provide numerous specific examples. You will note that TDI and MDI were reacted with a considerable number of trials and that various types of fluids were used in amounts from 20 to 80% of the total weight. This demonstrates that not only Aroclors are operable, but any fluid that is sufficiently compatible with the adduct or polymer may be used.

Although the solidifications successfully performed to date involved the use of elevated temperatures, we hope to so adjust the reactivity of the reaction mixture that a mild exothermic reaction will result which will cause the fluid reaction mixture to solidify shortly after being mixed and without the application of external heat.

Although the reactions and processes will undergo considerable refinement, we would like to have some coverage on the original, novel idea of solidification of fluids by polymerization of materials containing unreacted -NCO groups dissolved therein. It is felt that such a process would be useful in the following applications:

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E. P. Rucker
Anniston, Ala.

February 17, 1953

1. Casting or potting resins.
2. Solid dielectrics for capacitors or transformers.
3. Wire insulation.
4. Insulating varnish.
5. Adhesives.
6. Impregnation or surface treatment of porous materials to provide water resistance, flame resistance, improved hand, etc.

Our reason for requesting that you file on the basis of this incomplete information is that it is desired to give part of the pertinent knowledge to laboratories outside Monsanto in order to stimulate interest in isocyanates. We would not like to do this, however, until you have had the opportunity to examine the experimental results and file an application if you feel that we have a case.

The work referred to above will be found on the following notebook pages:

1. Original idea and extensions thereof:

82338; 84505; 84526, 27; 90105

2. Preliminary work with Aroclor, TDI, and triethanolamine. This work is unimportant except to serve as a basis for an early date:

82338-47; 82350 ✓
84510-13; 84519-22; 84531 ✓
✓ 78960-83; 78989-93; 78997-79000
85101-3; 85105-7.

3. Recent work of a more successful nature:

89901-7; 89910-35.
90101-5.

We will be glad to provide you with any additional information or assistance that we can.

H.L.H.
H. L. Heiss

HLM:kdl

PLAINTIFF'S EXHIBIT 61

**Correlation of Examples of U. S. Patent No. 3,102,875
With Experiments Reported in Notebooks of Defendant's
Exhibits**

Page 832a

CORRELATION OF EXAMPLES OF U.S. PATENT NO. 3,102,875
WITH EXPERIMENTS REPORTED IN NOTEBOOKS OF DEFENDANT'S
EXHIBITS

Example 1	-	p. 82342 8
Example 2	-	p. 78960 A
Example 3	-	p. 78982
Example 4	-	p. 78991 82342
Example 5	-	p. 84513
Example 6	-	p. 79000
Example 7	-	p. 78989
Example 8	-	p. 78991 88991 C
Example 9	-	p. 89925
Example 10	-	ps. 89901-02 89923 D
Example 11	-	ps. 89905 8991
Example 12	-	p. 89911 A 8991
Example 13	-	p. 89911 E-II
Example 14	-	p. 89913 A-J
Example 15	-	p. 89915 A, D-H, J p. 89916 89913
Example 16	-	ps. 89920, 21 89901, 8991, 89915
Example 17	-	p. 89927
Example 18	-	p. 89905G
Example 19	-	p. 89932 B, 89933, 89934, 89941
Example 20	-	p. 89929
Example 21	-	p. 89927 C

PLAINTIFF'S EXHIBIT 62

**Short Form Report No. 2: "The Preparation of Foams
From Polyols and Diisocyanates"**

**Work Started: April 10, 1953
Work Completed: April 30, 1954
Date Reported: May 6, 1954**

Pages 833a to 838a

RESEARCH AND ENGINEERING DIVISIONISOCYANATES PROJECTSHORT FORM REPORT

Report No. 2

Work Started: April 10, 1953

Work Completed: April 30, 1954

Date Reported: May 6, 1954

Job No. 117-2864

File No.

Investigators: J. H. Saunders
W. W. Robinson, Jr.
H. L. Heiss

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TITLE: The Preparation of Foams from Polyols and DiisocyanatesINTRODUCTION:

Since a number of polyols, such as those based on ethylene oxide, are potentially cheaper than polyesters, the preparation of foams from selected polyols was explored.

SUMMARY:

Both rigid and flexible foams were prepared from diisocyanates and a variety of polyols. Those foams prepared from ethylene oxide - and propylene oxide - derived polyols were greatly weakened by water. Foams from hydrogenated castor oil and polybutylene glycols were not affected greatly by water. All of these foams were weaker than the best diisocyanate-polyester foams of comparable density.

Foams from diisocyanates and castor oil were plasticized with Aroclor 1254 and with tricresyl phosphate.

CONCLUSION:

Rigid and flexible foams can be prepared from diisocyanates and polyols which are potentially cheaper than the polyesters now being used for foams. The polyol foams prepared thus far have been weaker than the best polyester foams, and many are water-sensitive. The flexible foams from the polyols did not support combustion. These foams show promise for applications where maximum strength is not required, but low cost is.

RECOMMENDATIONS:

It is recommended that the investigation of the less water-sensitive polyol foams be continued in more detail, including the addition of plasticizers.

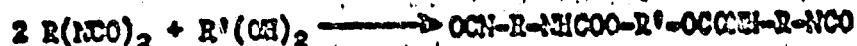
J. H. Saunders
J. H. Saunders

REFERENCE TO PREVIOUS WORK

Previous work on isocyanate-polyol foams was described in Interim Report No. E334, "Isocyanate Applications - Adhesives and Related Materials", by H. L. Poiss, February 3, 1953.

EXPERIMENTAL DATA:A. Method

Except where noted the "adduct" method of foaming was used. In this method diisocyanate and polyol are mixed in such a weight ratio as to give an excess of isocyanate groups over that amount equivalent to all of the hydroxyl groups. An NCO/OH ratio of 2:1 was used in this work, giving a reaction as indicated by the following equation.



This adduct, which contains both urethane groups and free isocyanate groups, is formed by the addition, with stirring, of water and a catalyst. The catalyst and water are stirred in during a few seconds to a minute at a temperature such that the adduct is fluid (25-70°). When foaming begins the stirring is stopped, and the foam is permitted to rise to its maximum height. After all foam has disappeared the foam is cured at 60-100° for a short time.

B. Polyethylene Glycol Foams

Early experiments with 2,4-TDI (tolylene diisocyanate) and PEG 400, 600 and 1000 (polyethylene glycols of the indicated molecular weights) showed that very weak foams resulted from these linear glycols. The introduction of varying amounts of the reaction product of glycerine and 0-9 moles of ethylene oxide (G-0-9 E.O.) as a cross-linking agent gave greatly improved rubberyness and resilience. Hence a cross-linking agent was used in subsequent foams.

Adducts were prepared from 2,4-TDI and PEG 600, 1000, 1540 and G-9 E.O. (reaction product of one mole of glycerine and nine moles of ethylene oxide), and from TDI mixed isomers (60% 2,4-, 33% 2,6-, and 1% other isomers) and PEG 600 and G-9 E.O. Adducts of the glycols and the triols were mixed as shown in Table I and were foamed with water and *N*-methylmorpholine as a catalyst.

TABLE I
POLYETHYLENE GLYCOL FOAMS

<u>Notebook</u>	<u>PEG Adduct, (g.)</u>	<u>Triol Adduct, g.</u>	<u>Water, g.</u>	<u>Catalyst, g.</u>	<u>Density, lb./cu.ft.</u>	<u>Resiliency</u>	<u>Hardness, 23°C.</u>
97023-1	600 (7)	3	0.22	0.09	6	Poor	Medium
97023-3	1000 (8)	2	0.27	0.09	5	Good	Soft
97023-1	1000 (7)	3	0.22	0.09	6	Good	Medium
103102-1	1540 (7)	3	0.53	0.20 ^a	5	Very Good	Medium
103102-4	4000 (0.7) ^a	1.83	0.21	0.21	5	Very Good	Firm

^a Mixed isomer adducts; others are from 2,4-TDI as *N*-methylmorpholine substituted for *N*-methylmorpholine.

The formulation represented by sample 97083-1 in Table I was nearly optimum for the PEG 1000 foams. Using higher and lower concentrations of triol adduct did not improve the foam. Higher concentrations of triol increased the firmness, while lower concentrations of triol gave weaker foams. The calculated polymer weight per branch point was 3300 for 97083-1, based on the triol as the only source of branching.

Substituting equimolar amounts of G.-6 E.O. and of G.-12 E.O. for the G.-9 E.O. in 97083-1 had little effect on the foam structure or properties.

The best PEG foams which were obtained were those from PEG 4000, G.-12 E.O. and mixed TDI (NB 105102). These foams did not shrink on curing, were soft and resilient at room temperature, and had fairly uniform cell structure. The foams melted at 268°.

All of the PEG foams were seriously weakened when immersed in water. Those foams with small cells lost nearly all of their tensile strength. Foams with coarser cells, and presumably thicker cell walls, were not affected so much.

Evidence was obtained to show that the PEG foams were hygroscopic and were plasticized by the absorbed water. One of the PEG 4000, G.-12 E.O., mixed TDI foams was fairly soft after several days in the freezing compartment (-10°) of the refrigerator. After refrigeration this foam weighed 2.77 g. After drying in a 135° oven the foam lost 0.6 g. and was stiff at -10°. However, after prolonged standing in the refrigerator the foam weighed 2.70 g. and was again soft at -10°.

C. Polypropylene Glycol Foams

Flexible foams were prepared from PPG (polypropylene glycol) 1200, the reaction product of glycerine and nine moles of propylene oxide (G.-0 P.O.), and 2,4-TDI in the same way as the PEG foams were made. The PPG polyols were substituted for the corresponding PEG polyols on a molar basis. Foams of 5 lb. per cu. ft. density were obtained which had average cell diameters of about 1 mm. with very few voids. These foams shrank approximately 10% after the maximum rise was reached. The PPG foams were less resilient than the PEG foams and were weakened by water only approximately one-half as much as the PEG foams. This weakening was still so pronounced, however, as to render these foams valueless when wet (NB 99S58).

During the course of this work it was observed that curing the PPG foams longer than 1 hour at 100° did not raise the melting point of the foam significantly. Thus after 1 hour cure the foam melted at 246°, and after 16 hours, 248°. This observation was assumed to mean that the foam was completely cured after 1 hour at 100° (NB 97039).

It was also found that foaming under pressure reduced the cell size markedly, and increased the foam density. Foams which were permitted to rise under 0.5, 20 and 30 psig. nitrogen pressure had large, moderate, small and very small cell size, respectively, and 3.3, 7.1, 10.6, and 12.7 lb. per cu. ft. density, respectively. (NB 97039).

Foams were prepared from PPG 750 and MDI (diphenylmethane diisocyanate); but these were dense, very tough and of low resiliency (NB 93460, 86, 97039).

A rigid foam of 5.4 lb. per cu. ft. density was obtained from a mixture of 18% PPG 400, 12% PPG 150, 18% G.-9 P.O. and 52% 2,4-TDI. For 10 g. of adduct mixture 0.32 g. of water and 0.09 g. of methylmorpholine were used in foaming. The compression strength was estimated at 100-150 psi. (NB 99967). A foam of 12.2 lb. per cu. ft. density was obtained from the same adducts when foaming was conducted under 30 psig. nitrogen pressure. The estimated compression strength of this sample was 250-280 psi. (NB 99967).

D. Polybutylene Glycol Foams

An 85:15 mixture of polybutylene glycol (PPG) 1000: G.-9 E.O. was mixed with 2,4-TDI at an NCO/OH ratio of 2:1 and was allowed to react. The calculated polymer weight per branch point was 4500. Using a 10-g. sample a foam was prepared by adding 0.21 g. of water and 0.28 g. of methylmorpholine. This foam rose to an initial density of 5.4 lb. per cu. ft., but shrank approximately 18%. The average cell diameter was 2 mm. This foam had poor resiliency, requiring 20-30 min. to recover its original shape after depression. (NB 103578-1).

The same adduct was heated for 15 hours at 100° to induce further branching via reaction of isocyanate and urethan groups. At the end of this time an amino equivalent analysis indicated that the average polymer weight per branch point had been reduced to 2800. This adduct was foamed as before, except that it was foamed at an initial temperature of 50° because of its high viscosity at room temperature. A foam of 8.2 lb. per cu. ft. density and no shrinkage was obtained. The average cell diameter was 0.5 mm., and the resiliency, though slow, was better than sample 103578-1 (NB 103578-2).

These polybutylene glycol foams apparently retained at least 80% of their strength when soaked in water.

E. Plasticized Castor Oil Foams

An adduct of Baker's All Castor Oil and 2,4-TDI was prepared in Aroclor 1254 using 33.8 g. of TDI, 66.2 g. of castor oil, 100 g. of Aroclor and 5 g. of methylmorpholine. This adduct was foamed with water and was cured for 15 min. at 100°. The adduct was also foamed using a methanol solution of benzyltrimethylammonium hydroxide (40%) as catalyst and source of gas. Presumably the gas was CO₂ from the base-catalysed decomposition of allophanate groups, arising from the reaction between isocyanate and urethan groups. The foams were fine-celled, flexible, and non-flammable, but had poor tensile strength (NB 92405).

Similar foams were prepared, substituting hydrogenated castor oil (Castor wax) for the castor oil. These foams were somewhat softer than those from castor oil. (NB 92406).

Tricresyl phosphate was substituted for Aroclor to give an odorless, non-flammable foam. This foam was weaker than the Aroclor-plasticized foams. Densities on these foams were about 16 lb. per cu. ft. (NB 97034).

F. Foams from Blends of Polyols

A series of foams was prepared from blends of PEG and PPG polyols. An adduct was prepared from 2,4-TDI and PPG 1200 plus G.-9 P.O. (NB 99058) and one from 2,4-TDI and PEG 1000 plus G.-12 E.O. (NB 97083 and 97089). The PEG and PPG adducts were mixed in 100:0, 50:50, 40:60, 20:80 and 0:100 ratios and were foamed. Densities ranged 3.4-6.8 lb. per cu. ft. As the PPG concentration increased the wet strength and hardness increased, while the resiliency decreased. Even the 100% PPG foam was weakened considerably by water (NB 103362).

A mixed adduct was prepared from 39 parts of hydrogenated castor oil, 28.6 of PEG 1000 and 32.2 of 2,4-TDI. This adduct, when foamed with 0.09 g. of methylmorpholine and 0.21 g. of water per 10 g. of adduct, gave a foam of 5 lb. per cu. ft. density. Resiliency was somewhat slow, 3 sec. being required to regain its original shape after compression. The wet foam had approximately 90-100% of the tensile strength of the dry foam. (NB 99931).

In an attempt to obtain other polyol foams of good wet strength hydrogenated castor oil was converted to a mixture of approximately equal molar concentration of diol and triol by treating it with octadecyl isocyanate. This mixture was then converted to an adduct with 2,4-TDI (60 parts of polyol, 29 of TDI) and was foamed. Using 0.22 g. of methylmorpholine and 0.53 g. of water for 10 g. of adduct a foam of 4 lb. per cu. ft. density was obtained. The resiliency was slightly better than the PEG 1000-hydrogenated castor oil foam, and the wet strength was equal to the dry strength. (NB 99976).

A polyester from adipic acid, ethylene glycol and propylene glycol, having an isocyanate equivalent of 1120, acid number 0.7, hydroxyl number 48.5 and water content 0.0% (Springfield NB 167673) was mixed with G.-12 E.O. and foamed by the adduct method. A mixture of 13 parts of G.-12 E.O., 66.6 of polyester and 20.4 of 2,4-TDI were used to make the first adduct. Ten grams of this adduct was foamed under 10 psig. nitrogen pressure, using 0.19 g. of methylmorpholine and 0.1 g. of water. A semi-elastic foam of 12.5 lb. per cu. ft. density and 0.3 mm. average cell diameter was obtained. When the polyester was foamed without the added triol a somewhat firmer foam was obtained at 12.8 lb. per cu. ft. density. Foaming the G.-12 E.O. without the polyester produced a hard foam of 8.8 lb. per cu. ft. density. The wet tensile strength of the polyester - G.-12 E.O. - TDI foam was about 50% of its dry strength. (NB 97089, 99975, 103565).

Mixtures of castor oil and PPG 750 were foamed with TDI and MDI to give foams of 3.7-9.8 lb. per cu. ft. density. These foams were soft to firm at 100°, firm at 25°, and rigid at -10°C. When wet they retained 80-90% of their dry tensile strength. (NB 93480).

G. Combustion Tests on Unplasticized Foams

A number of the unplasticized foams from the polyols did not support combustion. A summary of the burning experiments is given in Table II.

TABLE IIBURNING TESTS ON UNPLASTICIZED FOAMS

Notebook Page	Isoocyanate Used, % in Adduct	Polyols Used	Supports Combustion
103562-7	TDI, 45	G.-9 P.O. + PPG 1200	Yes
93480-4A	MDI, 42.3	Castor Oil	Yes
96967-2	TDI, 52	G.-9 P.O. + PPG 150 and 400	Yes
93480-4C	MDI, 40	PPG-750	No
97059-8	MDI, 40.8	PPG-750	No
90358-3	TDI, 30.9	PPG-1200 + G.-9 P.O.	No
99970-2	TDI, 29.4	ODI-Treated Castor Wax	No

* The adduct was branched by heat treatment, so 97059-8 was more highly cross-linked than 93480-4C.

In general, the flexible foams did not support combustion while the rigid foams did.

DISCUSSION:

The water-sensitivity of the PEG and PPG foams was doubtless due to the large number of ether links in each polymer molecule. Increasing the proportion of hydrocarbon content, as in PEG or by adding Castorwax, reduced the water sensitivity.

Many of the foams prepared thus far were desirably elastic at 100-125°, but were stiff at room temperature. Others which were soft and elastic at room temperature were stiff at -10° when dry. Certain of the PEG foams absorbed enough water to plasticize them, making them soft at -10°. Improvements in the low temperature flexibility will have to be made, as well as the water-sensitivity.

Controlling the reactions between TDI and PPG and PEG glycols was difficult. Hence this program was temporarily discontinued while more is learned about these reactions.

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